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A CRITICAL EXAMINATION OF THE USES
OF DIFFERENTIAL THERMAL ANALYSIS
IN THE FIELD OF POLYMER SCIENCE

by

J. J. SPARLING, B. Sc.

A THESIS

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled

A CRITICAL EXAMINATION OF THE USES
OF DIFFERENTIAL THERMAL ANALYSIS IN
THE FIELD OF POLYMER SCIENCE

submitted by J. J. Sparling, B. Sc., in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

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ABSTRACT

Differential thermal analysis was critically examined as the technique applies to the field of polymer science. The equipment and techniques for its use were investigated and the advantages and disadvantages of DTA for the measurement of first and second order thermodynamic transitions were evaluated. The interpretation of the thermogram for second order transitions was studied and an analog computer program set up for the heat transfer in a sample cylinder undergoing a glass transition. An attempt was also made to correlate the glass transition temperature of copolymers of styrene-butadiene and acrylonitrile-butadiene with their compositions.

It was found that DTA is a very effective and rapid technique, and the Aminco Thermoanalyser is a reasonably accurate piece of equipment for studying first and second order thermodynamic transitions occurring above ambient temperatures. It was also concluded that a number of modifications would have to be carried out on the Aminco Thermoanalyser to make it suitable for measurement of transition occurring below ambient temperatures.

The analog computer analysis for the DTA study of the glass transition indicated that the true transition temperature can best be obtained by extrapolating an indicated transition temperature versus heating rate curve back to zero heating rate. It was also felt that this program was a more accurate representation of the heat transfer in a sample undergoing a glass transition than any found in the literature.

A clear picture of the usefulness of the technique, used to try to analyse copolymers by means of their glass transition temperatures, was not obtained, because the glass transition temperatures of the copolymers studied were all below ambient temperatures and accurate thermograms could not be obtained.

TABLE OF CONTENTS

TABLE OF CONTENTS	i
LIST OF FIGURES	iv
LIST OF TABLES	vi
I INTRODUCTION	1
II POLYMER MORPHOLOGY	6
III POLYMER THERMODYNAMICS	13
A. First Order Transitions	14
1. Melting	14
2. Crystallization	15
B. Second Order Transitions	17
1. Glass Transition	17
2. Order-Disorder Transitions	19
C. Other Transitions	21
IV DIFFERENTIAL THERMAL ANALYSIS	22
A. The DTA Apparatus	23
B. Nature of the Thermograms	26
1. Heat Transfer in a Cylinder	26
2. The Thermogram	27
3. First Order Endothermic Transitions	28
4. First Order Exothermic Transitions	29
5. Second Order Transitions	29
C. Factors Affecting the Operation of the DTA Unit and the Results Obtained	32
1. Thermocouple Leads	32
2. Placement of the "Reference" or X Axis Thermocouple	32
3. Specimen Size	35
4. Heating Rate	35
5. Placement of the Furnace	35
6. Atmosphere	36
V DIFFERENTIAL THERMAL ANALYSIS OF POLYMERIC TRANSITIONS	37
A. First Order Transitions	37
1. Formation of the Peak on the Thermogram	37
2. Data Which can be Obtained from the Thermogram of a First Order Transition	41
3. Factors Affecting the Data Obtained from the Thermogram	48
4. DTA Studies of Polymeric First Order Transitions	49
B. Second Order Transitions	51

TABLE OF CONTENTS

V	DIFFERENTIAL THERMAL ANALYSIS OF POLYMERIC TRANSITIONS (cont'd.)	
	B. Second Order Transitions	
	1. The Thermogram for the Glass Transitions	51
	2. Data Obtained from the Thermogram	53
	3. Factors Affecting the Data Obtained from the Thermogram	54
	4. Studies of Polymeric Second Order Transition	59
VI	ANALYSIS OF POLYMERS BY DIFFERENTIAL THERMAL ANALYSIS	60
	A. Analysis of Polymer Systems Using the First Order Transition	61
	B. Analysis of Polymer Systems Using the Second Order Transition	64
VII	OTHER USES IN THE FIELD OF POLYMER SCIENCE	68
	A. Oxidation	68
	B. Decomposition	68
	C. Chemical Reactions	69
	D. Applications of DTA in Industry	71
VIII	EXPERIMENTAL	72
	A. Equipment	72
	B. The Melting Transition	79
	C. The Glass Transition	80
	1. Polystyrene	80
	2. Copolymers	81
	D. Interpretation of the Thermograms	84
	1. Model	86
IX	RESULTS	91
	A. Melting Point Determinations	91
	B. Glass Transition Determinations	95
	1. Polystyrene	95
	2. Copolymers	99
	C. Interpretation of the Thermograms	105
X	CONCLUSIONS	120
	A. The Aminco Thermoanalyser	120
	B. Uses of DTA for Examining First Order Transitions	121
	1. Difficulties Encountered	121
	2. Accuracy	122
	3. Usefulness	123
	C. The Uses of DTA in Examining Second Order Transitions	124
	1. Difficulties Encountered	124
	2. Accuracy	124
	3. Usefulness	125

TABLE OF CONTENTS

X	CONCLUSIONS (cont'd)	
	D. Interpretation of the Thermograms	125
	E. Uses of DTA for Polymer Analysis	126
	F. Uses of DTA of the First Order Transition for Polymer Analysis	126
	G. Uses of DTA of the Second Order Transition for Polymer Analysis	127
	H. Future of DTA in the Field of Polymer Science	127
XI	NOMENCLATURE	129
XII	BIBLIOGRAPHY	130

APPENDIX

LIST OF FIGURES

FIGURE NUMBER	TITLE	PAGE
1	Monomer Conformations	7
2	Polymer Conformations	11
3	Differential Thermocouple	22
4	Response of Differential Thermocouple, Sample Enthalpy, and Thermograms of Polymeric Transitions	30
5	Effects of Placement of the Temperature-Sensing Thermocouples on the Thermogram	34
6	Typical Thermogram of a First Order Transition	39
7	Thermogram Showing First Order Transitions of Polyethylene Terephthalate	42
8	Thermogram Showing First Order Transitions of Linear Polyethylene	43
9	Thermogram of Typical Second Order Transition	52
10	Effect of Heat Transfer Rate on Second Order Transitions	57
11	Effect of Short Chain Branching on Melting Temperature	62
12	Thermoanalyser Block	73
13	Aminco Thermoanalyser	76
14	Aminco Thermoanalyser	77
15	Gas Flow System of Aminco Thermoanalyser	78
16	Analog Simulation of Heat Transfer in DTA Apparatus	88
17	Typical Thermograms of the Melting Transition of Polymer P	92
18	Typical 'Complete' Thermogram of Polymers P and Q	93
19	Typical Thermograms of the Glass Transition of Copolymers	94
20	Typical Thermograms of the Glass Transition of Polystyrene	96
21	Sample: - Dow 683 Polystyrene	100
22	Sample: -Dow 683 Polystyrene	101
23	Typical Thermograms of the Glass Transition of Copolymers	102
24	Analog Simulation of Thermograms of the Glass Transition of Polypropylene	106
25	Analog Simulation of Thermograms of the Glass Transition of Polystyrene	107
26	Effect of Heating Rate on Indicated Glass Transition Temperature (Analog Simulation)	108
27	Effect of Heating Rate on Indicated Glass Transition Temperature of Polystyrene Sample	110
28	Analog Simulation of the Effect of Using the Sample Temperature to Drive the X Axis	112
29	Effect of Heating Rate on Indicated Glass Transition Temperature of Polystyrene-Butadiene Copolymers	113
30	Effect of Heating Rate on Indicated Glass Transition Temperature of Polyacrylonitrile-Butadiene Copolymers	114
31	Glass Transition Temperatures of Styrene-Butadiene Copolymers	116
32	Glass Transition Temperatures, Ethylene Propylene Copolymers	117

LIST OF FIGURES

FIGURE NUMBER	TITLE	PAGE
33	Glass Transition Temperatures Acrylonitrile -Butadiene Copolymers	118
34	Correlation of Glass Transition Temperatures with Composition for Polystyrene-Butadiene Copolymers	119

LIST OF TABLES

TABLE	TITLE	PAGE
A	Effect of CO Copolymer Units on the Melting Temperature of Polyethylene	53
B	Effect of CHCH ₃ Copolymer Units on the Melting Temperature of Polyethylene	63
C	Composition of Copolymers	82
D	Diluent Content in Styrene-Butadiene Copolymers	82
E	Results of DTA Melting Point Determinations	91
F	Results of DTA Glass Transition Temperature Determinations	97
G	Effect of Sample Weight on DTA Glass Transition Point Determinations	98
H	Molecular Weight Determinations for Polystyrene	98
I	Glass Transition Temperatures of Butadiene-Acrylonitrile Copolymers	103
J	Glass Transition Temperatures of Butadiene-Styrene Copolymers	104

I. INTRODUCTION

Plastic goods are in very common usage today and the plastics industry, from the synthesis of the raw materials through compounding and molding to the finished goods, is becoming increasingly complex. In all areas of the industry the physical, mechanical, optical and thermodynamic properties of the polymers must be known to allow for the fullest possible use of equipment and techniques, and to enable the best possible product to be marketed. Energy requirements are an important consideration in almost all processes involved in the various phases of the industry, and thus the thermodynamic properties of the polymers are very important. The most important thermodynamic effects are those which result in a change of form in the polymer (e.g. from solid to liquid, or from brittle to rubbery). These effects are referred to as thermodynamic transitions. It is essential in many techniques to know the temperature or temperature range at which these transitions occur.

The physical properties of plastic items produced from the molten polymer can be controlled by controlling the crystalline-amorphous ratio in the finished items. This can be accomplished by correct control of the melting and cooling techniques used in the manufacture of the items. A knowledge of the melting and crystallization phenomena of the polymer can lead to proper control of the manufacturing process.

In amorphous polymers, a knowledge of the glass transition point is very important in the end use of the product. Automobile tires must always be used above the transition point, otherwise they will become brittle and crack. On the other hand, a number of items are molded of amorphous polystyrene and are used below their transition point because strength, brittleness and durability are the desired properties for

these items.

Measurements of thermodynamic transitions are also used in polymer analysis. The transition temperatures, duration and related thermal effects are unique for each polymer system. The prediction of the components of copolymers, block and graft polymers and polymer diluent systems has been accomplished to a reasonable degree of accuracy (the accuracy varies with the equipment, the technique, the polymer system analysed and the operators) using thermodynamic properties.

A number of different techniques are available for examining thermodynamic transitions in polymers. Some of the more common ones are:

1. Stress Relaxation and Strain Relieving (93)

The relaxation of an applied stress is measured against time for a number of different temperatures. A plot of the time needed to reach a certain percentage of recovery v.s. the ambient temperature, shows a break at the transition temperatures. A modification of this technique involves the measurement of strain relief from an applied stress as a function of temperature. This is a dynamic technique.

2. Mechanical Damping or Dynamic Mechanical Analysis (56)

The changes in the Dynamic Young's Modulus of a vibrating reed of the polymer are measured against ambient temperature. Peaks in the plot indicate the transition temperatures. This is also a dynamic technique.

3. Dielectric Loss (105)

The changes in dielectric loss of silver plated polymer plates are measured for various frequencies and temperatures. Transition points are indicated by breaks in the dielectric loss, temperature curves produced.

This is a dynamic technique.

4. Torsional Braid Analysis (TBA) (32)

A glass braid coated with the polymer supports a pendulum. The damping of the pendulum is measured as a function of temperature -- a dynamic technique.

5. Thermal Gravimetric Analysis (TGA) (63)

In this technique the weight loss of the polymer is measured as a function of temperature. A break in the resultant curve indicates the transition temperature, -- a dynamic technique.

6. Dilatometry (73)

This technique examines the change in volume of the polymer brought about by changes in temperature. The changes in volume are measured at equilibrium, i. e. the temperature is changed and the system allowed to come to equilibrium before the volume change is measured. Breaks in the volume, temperature curves indicate transitions.

7. Calorimetry (15)

In this technique, the change of enthalpy of the polymer with temperature is recorded by measuring the heat input into the calorimeter as the temperature is varied. This is also an equilibrium technique.

8. Differential Thermal Analysis (DTA) (86)

Whenever a material undergoes a thermodynamic transition a change occurs in the enthalpic response of the material to temperature changes (heat is absorbed or given off, or the thermal diffusivity changes). In DTA, these changes in the enthalpic response are measured as differences in temperature

between the sample and an inert reference material, as the temperature of both are gradually increased. Breaks in the ΔT , temperature curves indicate the transitions. This is a dynamic technique.

DTA appears to be one of the most promising techniques for the study of polymer thermodynamic transitions. The first three techniques require that a range of tests at each temperature be carried out and these tests be repeated for a number of temperatures. Thus the study is quite time consuming. TBA is a very new technique and as yet has not shown sufficient accuracy for exacting thermodynamic studies. TGA is limited to transitions which exhibit a weight change, such as decomposition. Dilatometry and calorimetry, being equilibrium techniques are quite time consuming. Also the changes which occur in industrial processes are dynamic, not equilibrium types. Therefore, because of the rapidity of the tests, the similarity to actual industrial situations, and the accuracy of the technique, DTA is a most promising technique.

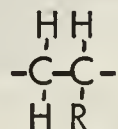
It is the purpose of this work to:

1. Review the literature for applications of DTA in the polymer field and to analyse its usefulness in these areas.
2. Investigate the advantages and disadvantages of DTA equipment and techniques.
3. Investigate the uses of DTA for measuring various polymer transitions with emphasis on the glass transition, because very little work has been carried out in this area.
4. Study the interpretation of thermograms, again with emphasis on the glass transition.
5. Attempt to analyse copolymer systems by using DTA to measure the glass

transition temperature, and comparing these values with theoretically predicted curves relating the glass transition temperature of the copolymer with its composition.

II. POLYMER MORPHOLOGY

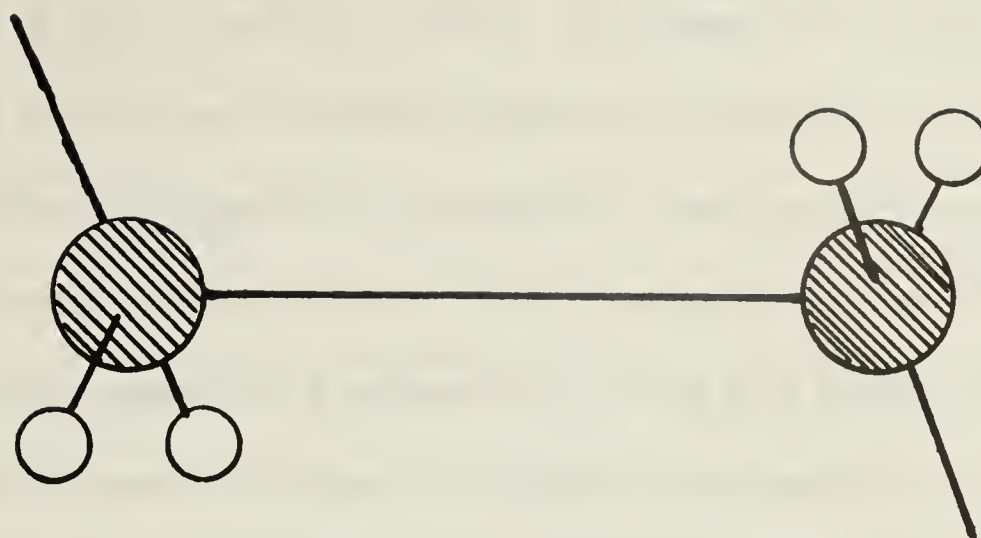
In order to discuss thermodynamic transitions, which are the result of changes in polymer structure due to motion of the molecules, a brief discussion of the molecular structure of polymers is necessary. A polymer molecule is made up of literally thousands of small repeating units or monomers. For simplicity, polyvinyls, with the monomeric structure



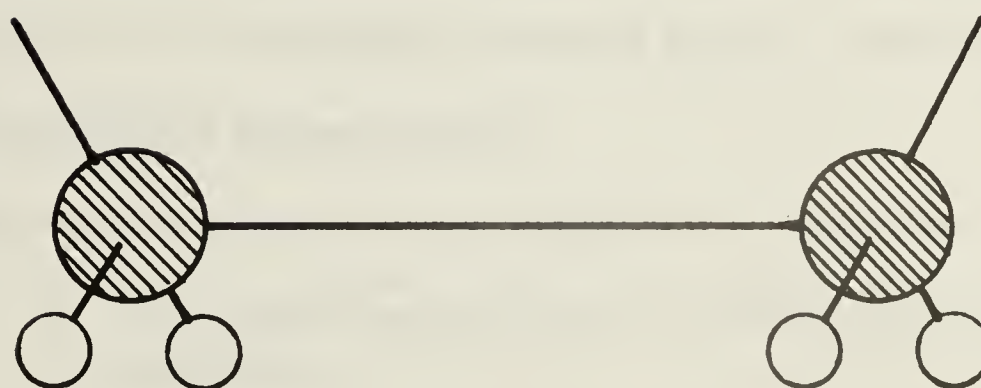
(R is any side group other than hydrogen)

In the following discussion the two terms configuration and conformation are defined as follows: configurations refer to spacial arrangements of atoms which cannot be changed unless the bonds joining them together are broken, while conformations are spacial arrangements which arise from bond rotation.

Now consider a single vinyl monomer. The two carbons have four covalent bonds each, at angles of $109^{\circ}30'$ from each other, thus forming a tetrahedron with the carbon atom in the middle. Two of these bonds are used in forming the carbon chain backbone structure and the other two are attached to the side groups. The carbon with the two H side groups is termed symmetric while the one with the R side group is asymmetric. This monomer has two possible conformations. Consider the carbon carbon bond as a horizontal line in space with two spheres representing the carbon atoms on either end of it. In the trans conformation the one carbon will have its two side groups above it while the other will have its two side groups below it. The two free bonds and the carbon carbon bond form a "chair" structure as shown in Figure 1. In the gauche conformation, the two free bonds and the carbon-carbon bond form a "dish" structure with both pairs of side groups below the carbon atom as shown in Figure 1. There are two gauche forms at $\pm 120^{\circ}$ rotation around the carbon carbon (C-C) bond from the trans form.



TRANS CONFORMATION



GAUCHE CONFORMATION

MONOMER CONFORMATIONS

FIGURE 1

Two of these monomers may join together in two different configurations, head to tail or head to head (tail to tail). In the head to tail configuration the sequence of carbon atoms is symmetric–asymmetric–symmetric–asymmetric, while in the head to head configuration two asymmetric or two symmetric carbons are together. These are the basic conformations and configurations for all types of polymers.

In larger segments of a polymer chain, three more configurations of the polyvinyl type of polymers can be seen. Consider a chain segment in the trans conformation and the head to tail configuration. If all the R groups are on the same side of the carbon backbone the segment is termed isotactic. If the R groups alternate regularly from side to side on the backbone, the segment is termed syndiotactic. An atactic segment is one with randomly oriented R groups. These three configurations are termed stereoregular polymer segments.

Other types of monomers may be classified into groups with:

1. two symmetric carbons with all four side groups the same as in polyethylene
2. two symmetric carbons with the side groups different as in polyvinylidene chloride
3. a symmetric and an asymmetric carbon containing three types of side groups as in polymethyl methacrylate.

Classification one has no configurations, as it appears the same no matter what arrangement it takes. It does, however, possess the trans and gauche conformations. Classes two and three possess the normal conformations and the head to tail or head to head configurations. Three also possesses stereoregularity. Some polymers, occurring by condensation polymerization, have oxygen and/or nitrogen as well as carbon in their backbone chains. Some elastomers contain some double bonds in the back-

bone.

Because the side groups in a trans conformation are within 2 to 5 angstrom units of each other (4), chain segments containing bulky side groups are often unable to form the trans conformations and must utilize a helical conformation to minimize bond strain. The tightest helix is formed by a regular sequence of trans and gauche bonds, giving three backbone units in a repeat. Bulkier side groups cause the helix to loosen up more. In other words, the rotation between two successive bonds is not 120° as in the trans gauche form, but some lesser degree of rotation. Polytetrafluoroethylene (PTFE), for example, has only a 20° rotation between successive backbone bonds and has 13 CF_2 groups in a repeat.

The term chain segment has been used in all the above descriptions because a polymer molecule may contain segments of different conformations and configurations. Thus, the polymer properties must be the statistical average of the properties of these chain segments.

The polymer chain described previously, with a regular occurrence of side groups along the whole molecular chain is termed a linear molecule, and is a rarity in polymer morphology. More often the chain is branched at various places along its length. These branches are random side groups longer than the normal side groups on the chain. Short branches are of the order of two to ten times the length of the normal side groups, while long branches are of the order of the main chain in length. If branches or normal side groups in two molecules should join together the molecules are termed cross-linked.

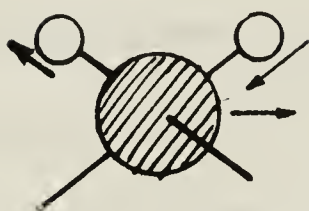
The configurations of a polymer molecule are fixed, but the conformations are constantly changing when the molecule has enough energy to move. The config-

urations impose limits on the changes in the conformations. Consider a molecule at a low energy level so all atoms are stationary. As energy is added, the atoms of the side groups begin to vibrate and rotate. Figure 2 shows the motions of the side groups and backbone of a polyethylene molecule according to Wunderlich (105). These motions do not change the conformations of the molecule. As more energy is put into the system, the energy barriers between the trans and gauche conformations are overcome and rotation of the backbone atoms results, usually from the gauche to the trans form, as the latter has the lower energy level. In a linear chain, these rotations cause the chain to wriggle, while in a helix, the motion is much like the compression and stretching of a spring.

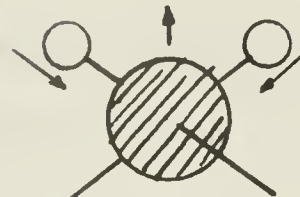
The polymer can exist in three different states, the disordered or amorphous, the glassy and the ordered or crystalline state. Decomposition occurs before temperatures, at which a gaseous form could exist, are reached. In the amorphous state the molecules are in motion and the polymer may be thought of as a viscous liquid. Molecular motions such as the vibration and rotation of the side groups, the elongation and relaxation of the backbone bonds and the rotation of the backbone units, are slowed as the temperature of the system is reduced. When the motion of the main polymer chain ceases, the polymer system is said to be in the glassy state, if a measure of the disorder found in the amorphous state is carried over into the solid state. If the environmental and internal conditions are suitable, the polymer molecules are able to reorient themselves into regions, termed crystallites, possessing a higher degree of order than the amorphous and glassy states.

The structure of crystallites has received a great deal of study in recent years. The general picture now agreed upon is that crystallites have the appearance of thin

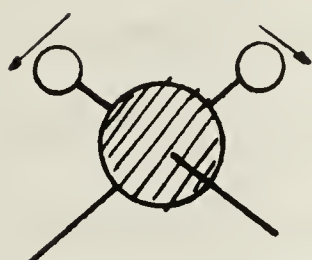
Stretching
(Asymmetric)



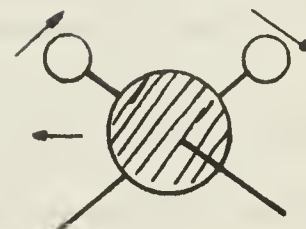
Stretching
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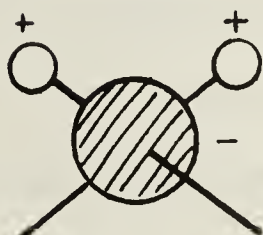
Bending



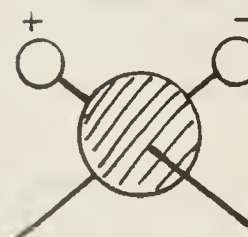
Rocking



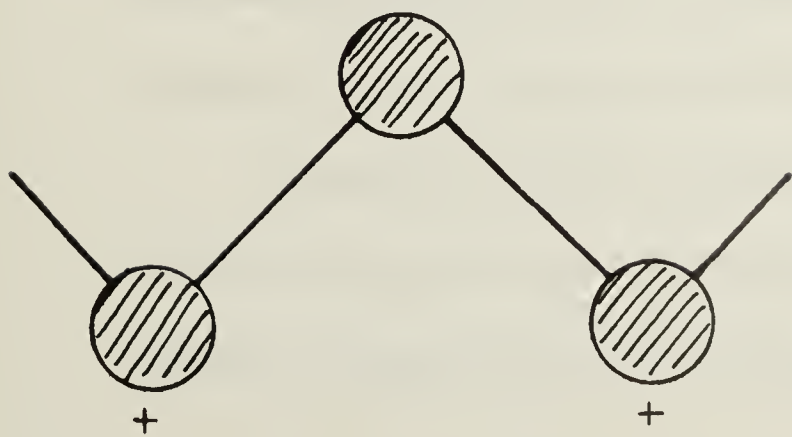
Wagging



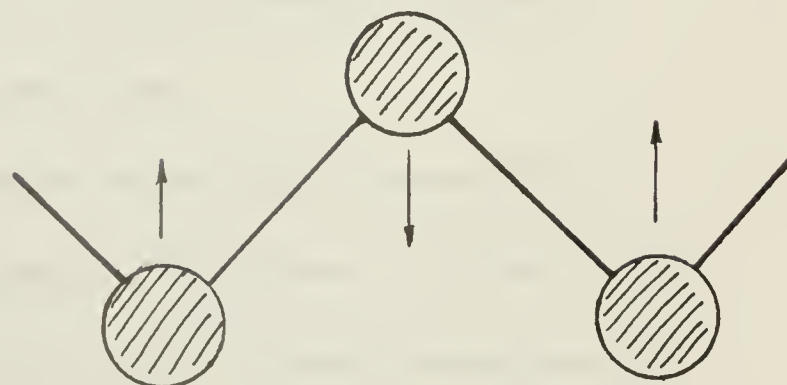
Twisting



Twisting



Bending



POLYMER CONFORMATIONS
FIGURE 2

rectangular plates made up of folded polymer chains, with the folds occurring perpendicular to the face of the plates. One school of thought (4,58,105) states that the chain lengths follow a regular sequence with the folds being a regular surface phenomena. Mandelkern (60), after a thorough study of the available information, has put forward a model in which the folds are not in a regular sequence; rather the chain segments all leave the ordered crystalline region and meander around an amorphous region on the surface of the crystallite. Some return to the crystallite region at a more distant point, others go into ordered regions of other crystallites and others remain in the amorphous region. This model is very close to the classical model of sections of parallel and sections of random chains. Thus the polymer is seen to be made up of ordered crystalline regions in a matrix of disordered or glassy material. These crystallites join together to form minute microscopic spherulites which can be recognized by their characteristic maltese cross pattern under a polaroid microscope.

More energy is necessary to cause motion in crystallites than in disordered regions because van der Waal's forces between adjacent and parallel chain segments impede movement. Thus the phase transition from the ordered crystalline to the disordered amorphous state is one necessitating a high input of energy. The more ordered the crystallite packing, the higher the energy input.

Changes in the mode and amount of molecular motion are accompanied by changes in the physical and thermodynamic properties of the polymer. It is these property changes which are the starting point for the study of polymer thermodynamics.

III. POLYMER THERMODYNAMICS

At absolute zero there is, theoretically, no molecular motion. Many extensive thermodynamic properties, such as enthalpy, entropy, free energy and specific heat all have zero values; while intensive thermodynamic properties, such as pressure, temperature and specific volume all have minimal values. On addition of heat the components of the molecule begin to vibrate, and, in the case of polymers, the chains begin to flex, and, if the heat input is sufficient, to rotate changing their conformations. The thermodynamic properties are also seen to increase with increasing temperature and molecular motion.

Specific heat of polymers has been statistically linked to molecular vibrations and rotations in a number of works (14, 95, 96, 97, 98, 103, 109). The increase in the extensive properties (enthalpy, entropy, specific heat and volume) is approximately linear over most of the temperature ranges, but at certain temperatures discontinuities occur in the property - temperature relationships which correspond to transitions in the polymer. These transitions have been divided into groups or orders by the types of discontinuities in the properties. Ehrenfest (22) set up the following criteria:

First order transitions result in discontinuities in the properties which are the first derivatives of G , the Gibbs Free Energy function,

$$\text{i.e. } (\partial G / \partial T)_p = -S = \Delta H / T; (\partial G / \partial p)_T = v$$

Second order transitions result in discontinuities in the properties which are second order derivatives of G ,

$$\text{i.e. } (\partial^2 G / \partial T^2)_p = C_p / T; (\partial v / \partial T)_p; (\partial v / \partial p)_T$$

Similarly, third and higher orders of transitions may be defined, but they are quite rare in actual systems.

A. FIRST ORDER TRANSITIONS

First order thermodynamic transitions are identifiable by the resulting reversible change of phase which occurs. They result in a change in molecular order of the material (e.g. crystal to liquid) and are the result of a change of internal energy in the material, caused by a change in the environment. The crystallization, melting and evaporation phenomena are the most common examples of first order transitions. Evaporation is of no concern in the field of polymer thermodynamics as the polymer decomposes before the evaporation point is reached. Studies of the melting and crystallization phenomena provide information about the molecular structure of the polymer and provide necessary process data on the polymers.

1. Melting

A polymer crystal is made up of closely packed, parallel chain segments bound together by van der Waal type forces. As energy is absorbed by a polymer molecule, the side groups vibrate and the chain segments try to rotate. Motion is hindered by the inter-chain forces in the crystal. Under certain specific environmental conditions, the forces tending to create chain motion overcome the interchain attraction forces, allowing the chain segments to move and causing the crystallite to break up. This is the melting transition and occurs as a molecular change from the ordered crystalline to the disordered amorphous, liquid state.

The degree of packing and the intensity of the interchain attractive forces

depend upon the chemical and physical structure of the chain (i.e. the types of side groups present, the chain length and the degree of branching, both short and long) and upon the length of the chain segments in the crystal, (i.e. the crystal thickness). (Peterlin and Fisher (75) and Peterlin, Fisher and Reinhold (76) have developed a thermodynamic theory of an optimum chain segment length present in a crystallite.) Thus the melting point is very dependent upon these same factors. For example, polytetrafluoroethylene (PTFE) has a melting point of 327°C . (60), while polyethylene has a melting point of 137.5°C . (60), chiefly because of the differences in inter-chain attraction between the F side groups and the H side groups.

2. Crystallization

Two types of crystallization are possible in polymers. One is the crystallization from the melt and is essentially the reverse phenomenon to melting. The second type is crystallization of the amorphous phase upon heating below the melting temperature. The latter is usually termed "cold" or "pre-melt" crystallization.

a. Crystallization from the Melt

In the melt, the polymer molecules are in continual, individual motion. They are most likely tangled and intertwined, but there are no lasting inter-molecular attractions present nor any lasting order of the molecules present. Many of the molecules may align themselves into positions favorable to the formation of crystallites, but the molecules contain too much energy and the intermolecular forces are broken as quickly as they are formed. If the environment is changed to conditions suitable for crystallite formation (usually

by lowering the temperature or increasing the pressure), the intermolecular forces which result from chance alignments hold the chain segments together causing the chain motion to slow or cease, and minute crystallites are formed. It is now easier for more chain segments to become ordered with these already aligned crystallites, causing them to grow.

If the rate of crystallization at constant pressure is examined for temperatures between the melting point and the glass transition point, assuming even cooling, a Gaussian type distribution is observed. At temperatures just below the melting point, molecular motion is rapid enough that a number of chain segments, which are properly aligned, become unaligned before the intermolecular forces can subdue the motive forces. Also there are few small crystallites to act as crystallization initiators. As the polymer is cooled the molecular motion slows and there is less chance of the intramolecular bonds being broken. Also the crystallites tend to initiate the growth of even more crystallites. However, after a certain point the reduction in molecular motion means that fewer and fewer chain segments are able to attain the correct positions for crystallization. At the glass transition point, changes in molecular conformations cease so no more molecules are able to obtain the degree of order necessary to form crystallites. The order of packing decreases as the temperature of crystallization decreases. At temperatures just below the melting temperature the molecules are so mobile that only alignments which produce the maximum possible intramolecular forces are able to overcome the chain motion, thus forming perfect, or almost perfect crystallites. As the temperature is lowered and

the molecular motion reduced, weaker forces are able to cause molecular motion to cease and less "perfect" crystallites are formed.

b. Cold or Premelt Crystallization

Molecular motion does exist in the amorphous region of the polymer at temperatures above the glass transition temperature. This motion is usually very sluggish, but often nearest neighbour segments of polymer molecules are able to align themselves to form small crystallites. The order and size of the crystallites are quite small and the crystallization rate is quite low.

B. SECOND ORDER TRANSITIONS

While first order transitions in polymers occur between the ordered, crystalline phase and the disordered liquid amorphous phase, the second order transitions occur only in one phase and thus do not exhibit the magnitude of change in molecular order that the first order transitions show. Two types of second order transitions are exhibited in polymers, both in the amorphous state. These are referred to as the glass transition and the order-disorder transition.

1. The Glass Transition

When an amorphous polymer is heated from a very low temperature, a transition occurs below which the polymer appears glassy and hard, and above which the polymer appears soft and rubbery. This is termed the glass transition, and is believed to occur under certain environmental conditions which initiate changes in the molecular conformation. Usually the temperature

is the main environmental variable, and will be treated as such here; therefore it can be said that the glass transition occurs at a glass transition temperature, T_g . Below T_g only molecular vibrations and side chain movements occur, above T_g molecule rotation also occurs, i.e. at T_g the molecule has sufficient energy to overcome the barrier between the trans and gauche conformations. It has been argued (4, 93, 103) that the changes occurring at T_g are not thermodynamically reversible, but are only kinetic effects causing an apparent transition with respect to the time scale of the measuring means. These authors argue that chain rotation occurs at temperatures down to absolute zero, but that they are so slow and occur in so few molecules that they cannot be measured below T_g . This is not the general view given in the literature, and as a certain energy barrier must exist between the trans and gauche forms of the polymer chain the view of a definite, reversible transition temperature seems the natural one to accept. In either cases, however, a transition is recognized by the measuring means we now possess. The glass transition can be recognized by a step change in the specific heat, a change in slope of a volume-temperature curve, a step in the thermal conductivity of the polymer, a break in the dielectric loss-temperature curve or a break in the stress or strain relaxation characteristics of the resin. Depending upon the time scale and accuracy of the means used to measure these properties, the transitions may appear to occur at a specific temperature or over a range of temperatures.

Theoretically the glassy state of the polymer is assumed to be one of "frozen" molecules with voids frozen into the molecular matrix. This void hypothesis is the

starting point for most theories predicting the glass transition temperature and the effect of various external and internal factors on T_g . Gibbs and DiMarzio (29, 30) give a quantum and statistical mechanical development of the partition function of a polymer molecule, built up on a model of occupied and vacant lattice sites. Using this partition function they show that there is indeed a discontinuity in the specific heat at the point where molecular motion starts or ceases. Hirai and Eyring (36) used a concept of photons and holes to explain the change in the specific heat at T_g . This theory was modified by Wunderlich (103, 106) to apply specifically to polymers. Wunderlich's calculated (calculated using literature data from 15 polymers) and experimental C_{p,T_g} values, were in quite close agreement (2.7 ± 0.5 and 2.97 cal./deg. mole). The classical Williams, Landel and Ferry (WLF) equation (100):

$$\ln(\eta_g/\eta) = 40 (T - T_g) / (52 + T - T_g)$$

where η_g is the viscosity of the polymer at T_g , η is the viscosity of the polymer at T , T is any given temperature and T_g is the glass transition temperature; was developed by Bueche (7) from a free volume - occupied volume model.

Factors such as cross linking, external pressure, high polarity and high molecular weight tend to reduce the free or void volume and thus raise the glass transition temperature. On the other hand, diluents, branches and co-polymers will increase the free volume and decrease T_g .

2. Order - Disorder Transitions

In metallurgy order-disorder transitions refer to changes in the crystal structure

of the metal. In polymer science the term is used with much the same idea in mind, only in polymers the change is one of molecular not crystalline structure. Examples of order-disorder transitions in polymers are the transitions at around 20 and 30°C. in PTFE in which the helix changes from one with 13 CF₂ units per rotation to one with 15 CF₂ units per rotation. Klug (54) suggests that the transition around 20°C. is caused by the molecular helices beginning to move in and out with respect to their neighbours in a sort of screw motion. The same transition is described by Eby and Sinnott (21) as a change from triclinic to disordered hexagonal packing and the uncoiling of the helix. The latter authors refer to the 30°C. transition as a further disordering of the hexagonal lattice to a form with an irregular repeating unit.

Although order-disorder transitions are not referred to as second order transitions in the literature they do exhibit a discontinuity in the specific heat over the transition temperature, which indicates a second order transition. There has been very little experimental work carried out on these transitions because of the difficulties involved in their measurements, as the heat effect of the transition is very small. One of the few thermodynamic studies of the order-disorder transition was carried out by Williams (100) on amorphous polyacetaldehyde. He used the WLF equation and the Gibbs and DiMarzio theory for glass transitions and found them applicable, within experimental errors, to the order-disorder phenomena. No record of any thermodynamic data on these transitions could be found.

C. OTHER TRANSITIONS

Changes in the thermodynamic and related properties of polymers with temperature changes have been observed below the glass transition temperature. These are believed to be due to the initiation of motion of side chains and branches. A transition has been found in polystyrene at approximately 50°C. (57, 64) which is around 50° below the glass transition temperature. This is likely the initiation of movement of the phenyl side groups.

Transitions in polymers with the $(\text{CH}_2)_n$ group have been studied by Wilbourn (99) using the technique of dynamic modulus. He discovered that three or more $(\text{CH}_2)_n$ groups on a side chain cause a transition at about -150° C. and four or more such groups in a chain cause a transition at around -100° C.

One other type of transition which has been observed results in a change of crystal structure in the polymer. Polybutene-1 is the best known polymer exhibiting this phenomena, and it shows three distinct crystallite structures(4, 93). Type I (M.P. 87° C.) is a rhombic crystal and is the most stable form, type II (M.P. 101° C.) is an unstable tetragonal crystal, while type III (M.P. 121.5°C.) has an unknown crystal form, but occurs upon crystallization from a solvent, and is unstable. The property changes affected by these transitions are very small and the difficulty of measurement has meant that very little is known of them to date.

Values of the thermodynamic properties of various polymers in the temperature ranges between transitions can be found from a number of works (1, 14, 15, 16, 18, 19, 37, 43, 62, 88, 95, 96, 97, 98, 103, 105).

IV DIFFERENTIAL THERMAL ANALYSIS

A rapid and quite accurate method of examining thermodynamic transitions, which is just starting to achieve its full potential as an analytic tool in polymer science, is differential thermal analysis (DTA). DTA measures the change in the **temperature of** the sample resulting from the change in thermal conductivity during the transition. This is accomplished by measuring the temperature difference between the sample and an inert reference material as both are heated equally, increasing their temperatures through the transition range of the sample. The sample and reference materials (hereafter referred to simply as sample and reference) are contained in symmetrically placed cells in a block. This block, usually a cylinder of metal with a high thermal conductivity, fits snugly into a furnace which in turn is encased in some type of insulation. The temperature difference between the sample and the reference in their cells is measured by a differential thermocouple (figure 3).

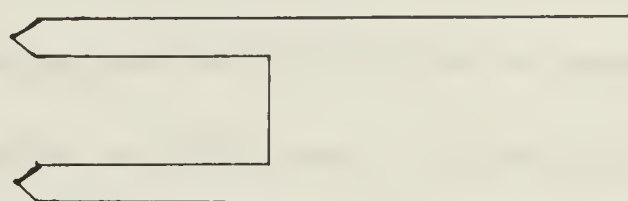


FIGURE 3 DIFFERENTIAL THERMOCOUPLE

When the signal from the differential thermocouple is amplified and fed to the Y axis of an X-Y recorder, and the X axis is driven by some reference temperature (usually the temperature of the block) the resulting graph is termed a thermogram. Thermograms give an idea of the enthalpic response of the sample to changes in temperature.

A. The DTA Apparatus

1. The Block

The block is usually cylindrical to provide the most even heat transfer to the cells. Blocks have been made from graphite, ceramic brick, alumina, aluminum, nickel, palladium, cast iron and stainless steel to mention the most common types. The merits of a good conductor versus a poor conductor from the standpoint of even heat distribution to the cells have been argued for a long time, but it has been decided that a good conductor is the best (86). Therefore most of the modern DTA units contain metal blocks.

2. The Cells

The cells are mounted symmetrically in the block to give an even heat distribution to the reference and the sample. Usually there are two cells in the block, but more have been tried in order to amplify the resulting temperature differences. However, this can lead to slightly different responses from each sample, causing a great deal of difficulty in interpreting the thermogram.

The thermocouples are positioned on the centerline of the cells and the sample and reference packed around them. These thermocouples may enter the cell from either the top or the bottom. If they are placed into the sample and reference from the tops of the cells, the positioning and reproducibility of the positioning of the thermocouples is often a problem. If they enter the cells from the bottom, they must be sealed so that liquid samples may not leak around them. This is often a problem in the very small cells used. The sample and reference are often contained in thin walled glass, platinum or steel cups to make cleaning of the cells easier. Sometimes these cups are

formed to fit over bottom entry thermocouples eliminating the problem of leaks, but incorporating a heat transfer barrier between the materials being tested and the thermocouples. This also means that the temperature measured by the thermocouple is not the true center temperature of the materials in the cells, but an average of the temperature profile across the material because of the heat transfer from the material to the cup.

3. The Furnace

Furnaces are usually constructed of ceramic tubes wound with a resistance wire element. They may be mounted either vertically or horizontally over the block. In one type of furnace, the linear differential furnace (20), the windings are spaced so that the temperature increases linearly along the length of the furnace. The block containing the reference and sample is moved along the length of this furnace at a steady rate, thus linearly changing the temperature and doing away with a programmer on the electrical supply to the furnace. However, the programmer is easier to build than a variable, linear drive for the block in the furnace.

Infra red heat lamps (72) have also been used to heat the materials in a specially designed block, but convection currents are developed in the air which makes using this furnace very difficult.

4. The Insulation

The furnace is insulated either by means of a layer of insulating material, such as an asbestos sleeve, or by a radiation shield. The latter creates a dead air space between the furnace and the shield and also reflects radiation back to the furnace.

5. The Programmer

The electrical input into the furnace is usually controlled by a motor driven variac to provide the linear heat input necessary for the furnace.

6. The Recorder

The most common type of recorder used is an X-Y plotter with the Y axis recording the temperature difference between the reference and sample, as measured by the differential thermocouple, and the X axis measuring the block temperature. Since the block temperature is, theoretically at least, linear with respect to time, some units have used the simpler Y versus time recorders. The resulting thermograms are not as accurate as those produced using an X-Y plotter. This is because the programmed heat input to the furnace is seldom completely linear with respect to time.

B. NATURE OF THE THERMOGRAMS

1. Heat Transfer in a Cylinder

A brief look at the heat transfer in a cylinder is necessary to understand and interpret a DTA thermogram of a polymeric transition. Consider an infinite cylinder of material having a thermal diffusivity k , with a radius a , whose surface temperature is increased at a constant rate β . At time $t = 0$ the temperature across the radius of the cylinder, r , is constant at $T = 0$. The Fourier equation for heat transfer through a cylinder in the radial direction

$(\partial T / \partial t = (1/r) (\partial T / \partial r) + (\partial^2 T / \partial r^2))$ was solved by Carslaw and Jaeger (9), for the above conditions, giving;

$$T = \beta (t - (a^2 - r^2) / 4k) + (2\beta / ak) \sum_{n=1}^{\infty} (J_0(r\alpha_n) / \alpha_n^3 J_1(a\alpha_n)) \exp.(-k\alpha_n^2 t) \dots 1$$

where J_n represents a Bessel function of order n and α_n is the n^{th} root of the equation $J_0(\alpha a) = 0$. For cylinders in which the radius, a , is small, only α_1 need be considered. The value of T at the center of the cylinder, T_o , for t quite large (i.e. at steady state) is given by:

$$T_o = \beta t - (a^2 \beta) / 4k \dots \dots \dots 2$$

Now consider the sample and reference cylinders in the DTA unit, with the sample not undergoing a transition. In applying equation 2 to these two cylinders, the only difference encountered in the two results is in the values of k . If the subscripts R and S represent the reference and sample respectively, then:

$$T_{oR} = \beta t - (a^2 \beta) / 4k_R \dots \dots \dots 3$$

$$T_{oS} = \beta t - (a^2 \beta) / 4k_S \dots \dots \dots 4$$

$$T_{oR} - T_{oS} = (a^2 \beta / 4) (1/k_S - 1/k_R) \dots \dots \dots 5$$

Therefore, at steady state under the conditions presented, the temperature difference between the centers of the two cylinders is constant. Prior to the attainment of steady state, the values of T_{OR} , T_{OS} , and T_O will be:

$$T_{OR} \approx \beta t - a^2 \beta / 4k_R (1 - \exp. (-k_R \alpha_1^2 t)) \quad \dots\dots\dots 6$$

$$T_{OS} \approx \beta t - a^2 \beta / 4k_S (1 - \exp. (k_S \alpha_1^2 t)) \quad \dots\dots\dots 7$$

$$\Delta T_O \approx (a^2 \beta / 4) (1/k_S - (1/k_S) \exp. (-k_S \alpha_1^2 t) - 1/k_R / (1/k_R) \exp. (-k_R \alpha_1^2 t)) \quad \dots\dots\dots 8$$

Thus ΔT_O is seen to rise asymptotically from zero to the steady state value given by equation 5.

This is an idealized picture of the heat transfer in each cell of the DTA apparatus when the sample is not undergoing a transition. In actual fact the cylinders are not infinite but usually have length to diameter ratios of from one to one to five to one. The cylinders are rarely homogeneous, and the heat transfer to the surface of a cylinder is not the same on all sides because the block is not a perfect conductor of heat. However, the picture presented above gives a good approximation of the heat transfer process and a more rigorous treatment is beyond the scope of this work.

2. The thermogram

Consider a DTA unit initially at steady state with no heat being applied to the block. The temperatures of the sample, reference and block are all the same. The axis controls of the X-Y plotter are set at some predetermined point. The unit is now turned on and heat is applied to the block. The reference and the sample heat at different rates, as indicated by equations 6 and 7, causing the ΔT_O value to rise asymptotically. The block

is simultaneously increasing in temperature. Thus the X-Y plotter responds by plotting a curve which rises steeply at first but levels off quite quickly. The ΔT_0 value at which the curve levels out is given by equation 5. This level value is termed the baseline of the thermogram. Any changes in the heat transfer characteristics of the sample (the reference is usually chosen to be completely inert through the analysis temperature range) will upset the equilibrium ΔT_0 value and thus produce a curve departing from the baseline on the thermogram.

3. First Order Endothermic Transitions

If a sample undergoes an ideal first order thermodynamic transition, heat is either absorbed or given off and the temperature of the material remains unchanged throughout the transition. When the sample in a DTA unit undergoes an endothermic first order transition, the heat input to the sample cell is absorbed and the sample does not change temperature. Meanwhile the same amount of heat input into the reference cell causes the temperature of the reference to increase linearly thus increasing the temperature difference between the reference and the sample. The increase of the temperature difference continues until the transition is complete. Then the temperature of the sample increases rapidly (the thermal diffusivity of the sample has increased) until a steady temperature difference is again obtained. On the thermogram, the increasing temperature difference registers as a drop from the baseline, and the decrease of the temperature difference as a sharp return to the baseline. By convention, the increasing temperature difference of the endothermic transition is registered as a drop on the thermogram so that the entire transition registers as a dip or downward peak (the term peak

is still applied) on the thermogram. The transition temperature is assumed to be the point where the transition ceases (all the sample has undergone the transition) and thus is indicated as the top of the peak produced on the thermogram. Figure 4 illustrates the thermogram of a typical endothermic first order transition, along with the enthalpic changes and the responses of the differential thermocouple.

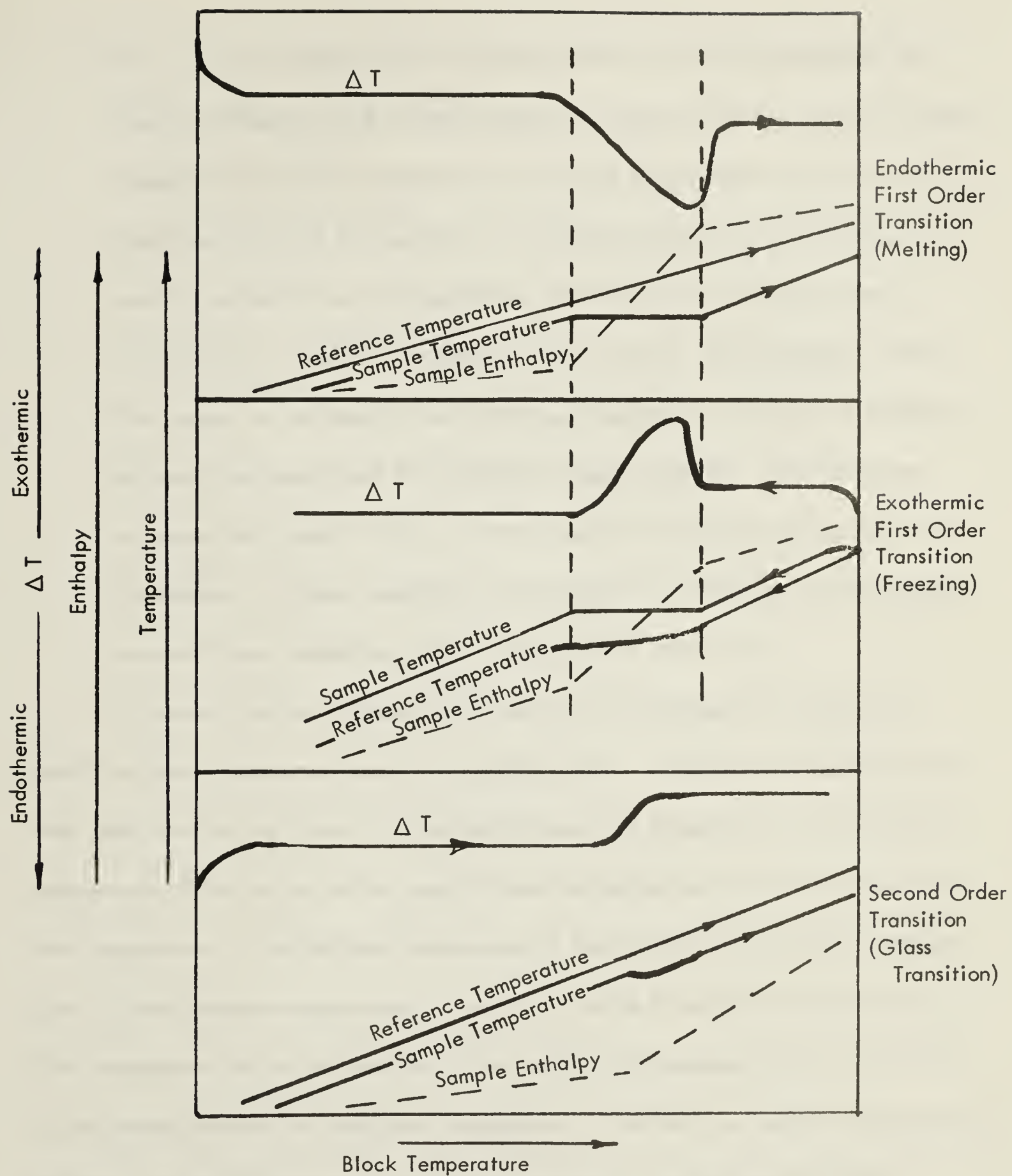
4. First Order Exothermic Transitions

Figure 4 illustrates the response of the sample and reference thermocouples, the enthalpic changes of the sample and the thermogram for a first order exothermic transition. It should be noted that the peak on the thermogram rises above the baseline in this case. After the initial baseline is established and the transition started, heat is given off by the sample and must be absorbed by the reference. Thus the peak has a sharp incline, caused by the arresting of the sample temperature, and a gradual decline caused by the heating of the reference by the heat from the sample.

The transition temperature for an exothermic transition is taken as the starting point of the transition and thus is indicated on the thermogram as the temperature where the peak first rises from the baseline.

5. Second Order Transitions

Figure 4 also shows the response of the two legs of the differential thermocouple, the enthalpic change of the sample and the thermogram for a sample undergoing a second order transition. In this case, heat is neither given off nor absorbed during the transition, but the thermal diffusivity of the sample changes. This results in a new thermal response of the sample after the transi-



RESPONSE OF DIFFERENTIAL THERMOCOUPLE, SAMPLE ENTHALPY,
AND THERMOGRAMS OF POLYMERIC TRANSITIONS

FIGURE 4

tion, so a new steady state temperature difference must be obtained. The thermal diffusivity of the sample usually is reduced when the sample is heated through the transition temperature, causing a longer time lag between the time the surface of the sample is at a certain temperature and the time the center reaches the same temperature. This change in heat absorption is indicated by a rise (by convention) in the curve on the thermogram. After the sample has undergone the transition, a steady state temperature difference between the sample and the reference is again obtained. The transition temperature is usually taken as the mid-point of the step-type curve on the thermogram. A more comprehensive analysis of the changes occurring during a second order transition will be discussed in a later section.

In actual fact, the temperatures taken from the thermograms as being the transition temperatures are usually only approximate. If the block temperature has been used to drive the X axis, the indicated transition temperature is actually the temperature of the surface of the sample when the center has reached the true transition temperature. The indicated temperature is thus higher than the actual temperature. If the reference temperature is used to drive the X axis, the indicated transition temperature is the temperature at the center of the reference, when the center of the sample reaches the transition temperature. Thus the true transition temperature depends upon the difference in the thermal conductivity of the sample and the reference.

C. FACTORS AFFECTING THE OPERATION OF THE DTA UNIT AND THE RESULTS OBTAINED

1. Thermocouple Leads

Thermocouple leads must attain a favorable balance between size and stiffness to be effective. The leads should be quite small to reduce the heat transfer along them to a minimum. However they should be stiff enough to ensure reproducibility of placement of the leads and to enable them to be placed as closely as possible to the center of the cells.

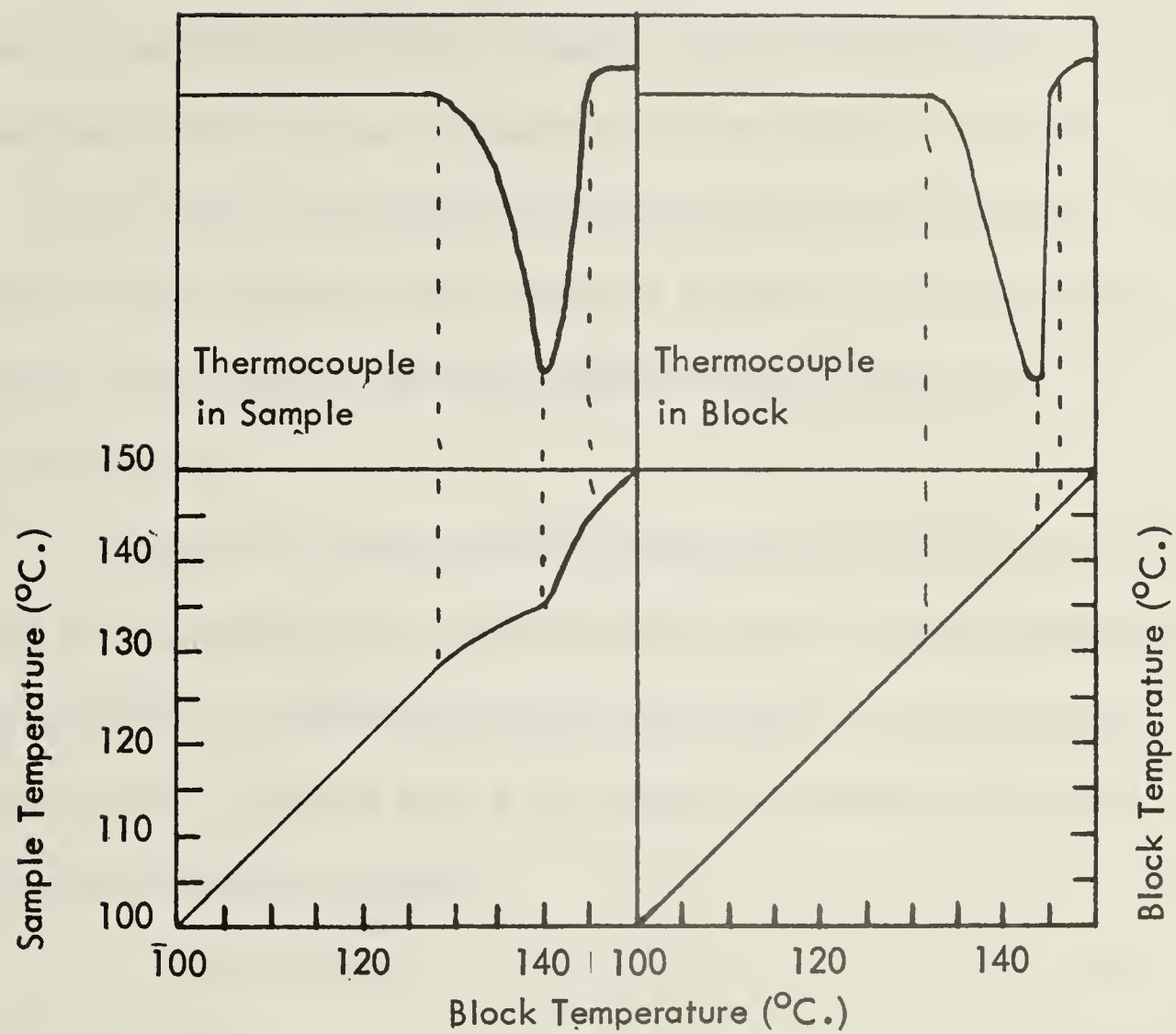
2. Placement of the "Reference" or X Axis Thermocouple

The thermocouple which drives the X axis of the recorder usually records the temperature of the block, or effectively, the temperature of the surface of the cells. In some cases, however, the system may be arranged so that either the sample or the reference leg of the differential thermocouple may be used as the X axis thermocouple. In other cases where it is desirable to use the reference (or the sample) temperature for the X axis temperature two thermocouples can be inserted into each cell. The second thermocouple in one of the cells is just a dummy to balance the heat transfer characteristics of the two cells. In the former system, one leg of the differential thermocouple must drive the X axis of the plotter and act as a part of the signal to the Y axis. This causes a shift in the ΔT_0 value of the thermogram (10) producing an unrealistic peak. In the latter case, the location of the two thermocouples leads to a great many problems and can also indicate an unrealistic peak. For example, if the thermocouple driving the X axis is in the center of the cell, the one which is a part of the differential thermocouple must be closer

to one side. Thus the value of ΔT_0 is not the true temperature difference between the centers of the sample and the reference. The locations of these two thermocouples in the cell would be extremely difficult to reproduce in a series of runs so the results are not reproducible.

For these reasons the block temperature is the commonly accepted X axis temperature.

Ke (49) conducted an experiment to show the effect of using the sample temperature to drive the X axis for the case of a polymer undergoing a first order endothermic transition. A second small thermocouple was embedded into the sample in each of two tests. In the first, the signal from this thermocouple drove the X axis, in the second the thermocouple was a dummy to make the heat transfer characteristics the same for each run and the X axis was driven by the block thermocouple. The resulting thermograms plus the curves of the X axis temperature versus the block temperature are shown in figure 5. It can be seen that the peak temperature is reduced and the shape of the peak is changed when the sample temperature is used for the X axis temperature. The reduction in peak temperature can be easily explained when one realizes that at any given moment during the test the temperature of the surface of the sample (the block temperature) is always higher than the temperature of the center of the sample due to the heat transfer lags. The difference in peak shape, however, can lead to difficulties in obtaining the transition temperature, as the return from the peak to the baseline is not sharp, therefore the use of the sample thermocouple to drive the X axis is conventionally ignored.



EFFECTS OF PLACEMENT OF THE TEMPERATURE-SENSING THERMOCOUPLE
ON THE THERMOGRAM

FIGURE 5

3. Specimen Size

The size or more correctly the quantity of sample and reference used affect the results of the DTA test. Larger quantities produce higher, broader peaks and higher peak temperatures in first order transitions (49, 82). On the other hand samples which are too small produce curve distortion due to poor resolution (82). Analysis of the effect of specimen quantity on second order transition thermograms (82) have been inconclusive.

4. Heating Rate

As a general rule, the faster the heating rate (or the cooling rate) the higher and broader the peaks, and the higher(or lower) the peak temperature. This can be seen by examining the heat transfer equations given previously: From equation 1, equations 2 and 9 shown below can be developed for the cases r equals zero and r equals a :

$$T_{r=0} = \beta t - a^2 \beta / 4k \quad \dots\dots\dots 2$$

$$\text{and } T_{r=a} = \beta t \quad \dots\dots\dots 9$$

Thus, if the block temperature is used as the X axis temperature, the difference between the actual temperature of the sample at a given point on the thermogram and that recorded on the X axis is:

$$T_{r=a} - T_{r=0} = a^2 \beta / 4k \quad \dots\dots\dots 10$$

which is dependent upon the heating rate β . The fact that the ΔT_0 is also rate dependent can be seen from equation 8.

5. Placement of the Furnace

If the furnace does not fit symmetrically over the block, one cell may receive more heat than the other causing an increasing or decreasing baseline

on the thermogram. This can happen quite easily if the furnace is quite long. A slight slope at the bottom of the furnace will cause a quite significant lean at the top of the furnace which will affect the resulting thermogram.

6. Atmosphere

Most DTA units operate with the block in a gaseous atmosphere. Often this atmosphere can be controlled as to the type of gas, the pressure of the gas and the rate of flow of the gas. The type of gas used is important in cases where the sample could react with one of the components in a gas stream such as oxygen. The oxidation peak produced can often mask other, more important peaks in the analysis. Stone (87) has shown that increasing the pressure increases the temperature at which various transitions take place. Schwenker and Zuccarello (82) have determined that peak heights are increased by a flowing rather than a diffusing atmosphere, but that the transition temperatures are not changed. No reason was extended for this phenomenon.

V. DIFFERENTIAL THERMAL ANALYSIS OF POLYMERIC TRANSITIONS

The previous section has outlined the basic principles of differential thermal analysis. These will be expanded here as they apply specifically to the uses of DTA in polymer science.

A. First Order Transitions

First order polymeric transitions cover melting, crystallization from the melt and a crystallization (termed "cold" crystallization or "premelt" crystallization,) which occurs below the melting point in amorphous regions of the polymers under certain conditions. The melting transition is endothermic while the two types of crystallization are exothermic.

1. Formation of the Peak on the Thermogram

a. The Endothermic or Melting Peak

The effects of the heat transfer lags in the DTA system and the different crystallite sizes in the polymer combine to give the endothermic peak on a DTA thermogram of a polymer being melted. Each is capable of producing the peak, and the amount of their individual contributions depends upon the cell dimensions and the polymer sample being tested. They will be described individually and then in their related state.

i. Heat Transfer Lag Mechanism (See figure 6)

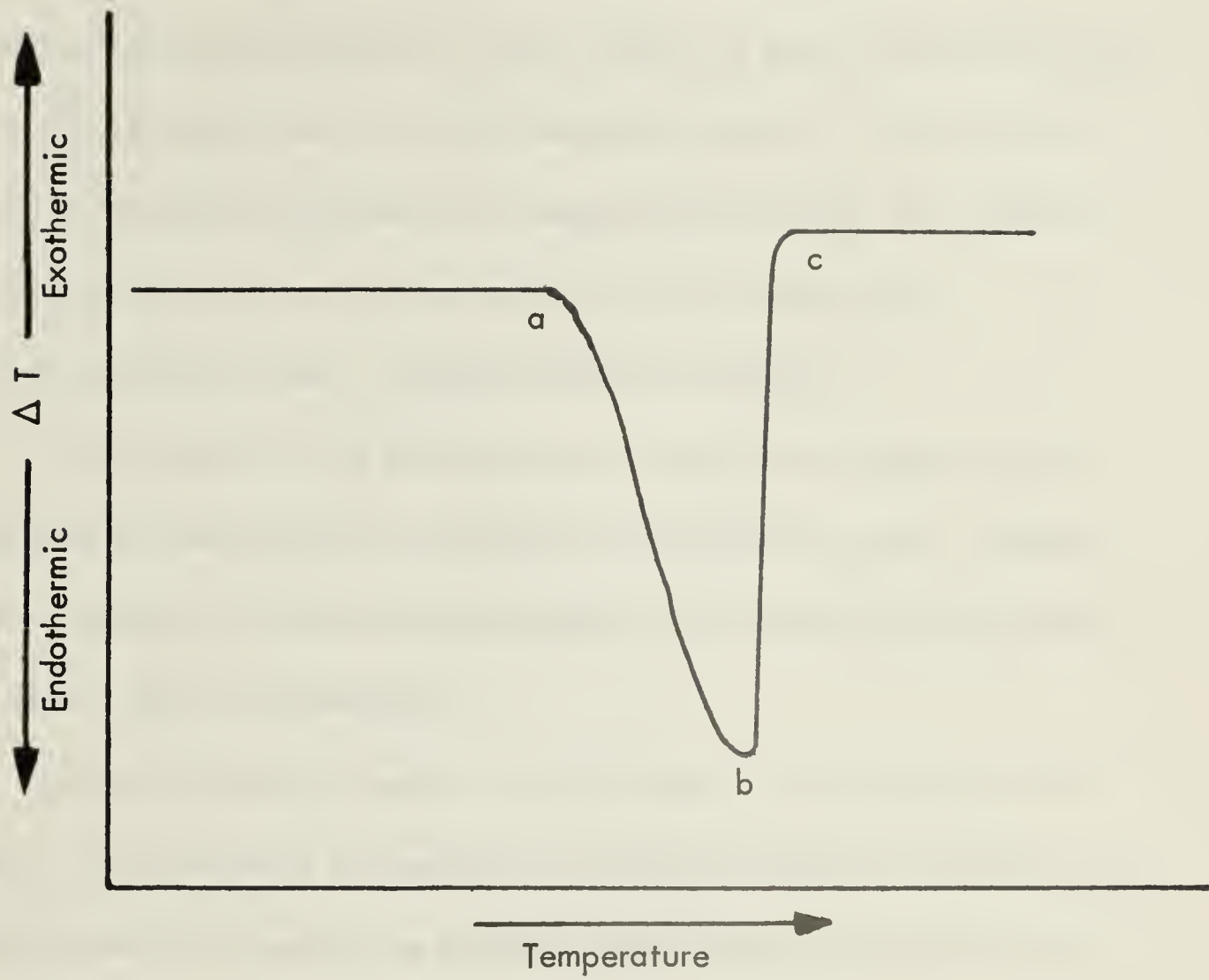
Consider that the cylindrical sample is divided into a number of annular layers. When the transition begins, the outer layer absorbs all of the heat going to the sample cell in order to undergo the melting transition. Thus no

heat reaches the thermocouple in the center of the cell and it remains at the temperature at which the transition started. When the outer layer of the sample has undergone the phase change, it will begin to increase in temperature while the next layer changes phase. Thus the temperature of the center of the sample where the thermocouple is located remains at the transition temperature until the entire sample has changed in phase, giving the endothermic curve "a-b". Then the center temperature increases and the temperature of the sample again approaches that of the reference giving the exothermic curve "b-c". Of course this phase transition is a continuous phenomena and does not actually occur in layers.

ii. The Crystallite Size Distribution Mechanism

The polymer contains vast number of crystallites, all of different sizes and degrees of packing and thus all melt at different temperatures. Therefore the peak formation can also be explained in terms of the melting of these crystallites. At temperature "a" the most imperfectly formed crystals begin to melt, absorbing all the heat and thus keeping the sample temperature constant. When they are all melted, the heat input goes to raise the sample temperature to the point where another group of crystallites melt. This continues until all the crystals are melted. The change would not be in steps as indicated but would be continuous because of the vast number of crystallites in varying sizes present in even the most minute sample possible for this type of analysis.

If the radial dimension of the sample is quite large the first mechanism will predominate, but if the radius of the sample cylinder is small the first



TYPICAL THERMOGRAM OF A FIRST ORDER TRANSITION

FIGURE 6

mechanism can be ignored and the second predominates. In either case, the effect of the crystallite size distribution influences the peak so that the point at which the melting ceases need not necessarily be point "b", but could be some point between "b" and "c", due to a more rapid heating of the semi-liquid sample than of the solid reference material. Thus the melting point of the polymer (defined as the temperature where the last crystallites melt) cannot usually be obtained exactly from the thermogram.

b. The Exothermic Peak - Crystallization from the Melt

The formation of the exothermic melt crystallization peak occurs by the same two mechanisms as those which form the melting peak. However, the mechanisms are altered slightly because of the exothermic phenomenon.

i. Heat Transfer Lag Mechanism

When the transition begins, the outer layer of the sample gives off heat. This counteracts the cooling of the block and heats the reference to a slight extent. The outer layer crystallizes and begins to cool allowing the next layer to crystallize. The heat given off by the inner layers is absorbed by the outer layers to a certain extent. It is also possible that the thermocouple at the center of the sample may be heated slightly by this heat of crystallization. These factors account, in part at least, for the difference in peak shapes between the melting and the crystallization peaks as indicated in the previous section.

ii. The Crystallite Size Distribution Mechanism

By cooling from the melt to below the melting temperature, conditions are reached at which polymer chains having the proper alignment will come

together to form crystallites. The chains will achieve the proper alignment in different parts of the sample at different times depending upon the configurations, conformations and chain length of the various molecules in the area. Thus crystallites are formed at different temperatures. (The block is being continuously cooled.) Heat is given off when each crystallite is formed thus keeping the temperature of the center of the sample at a constant temperature or else heating it slightly.

c. The Exothermic Peak - Cold Crystallization

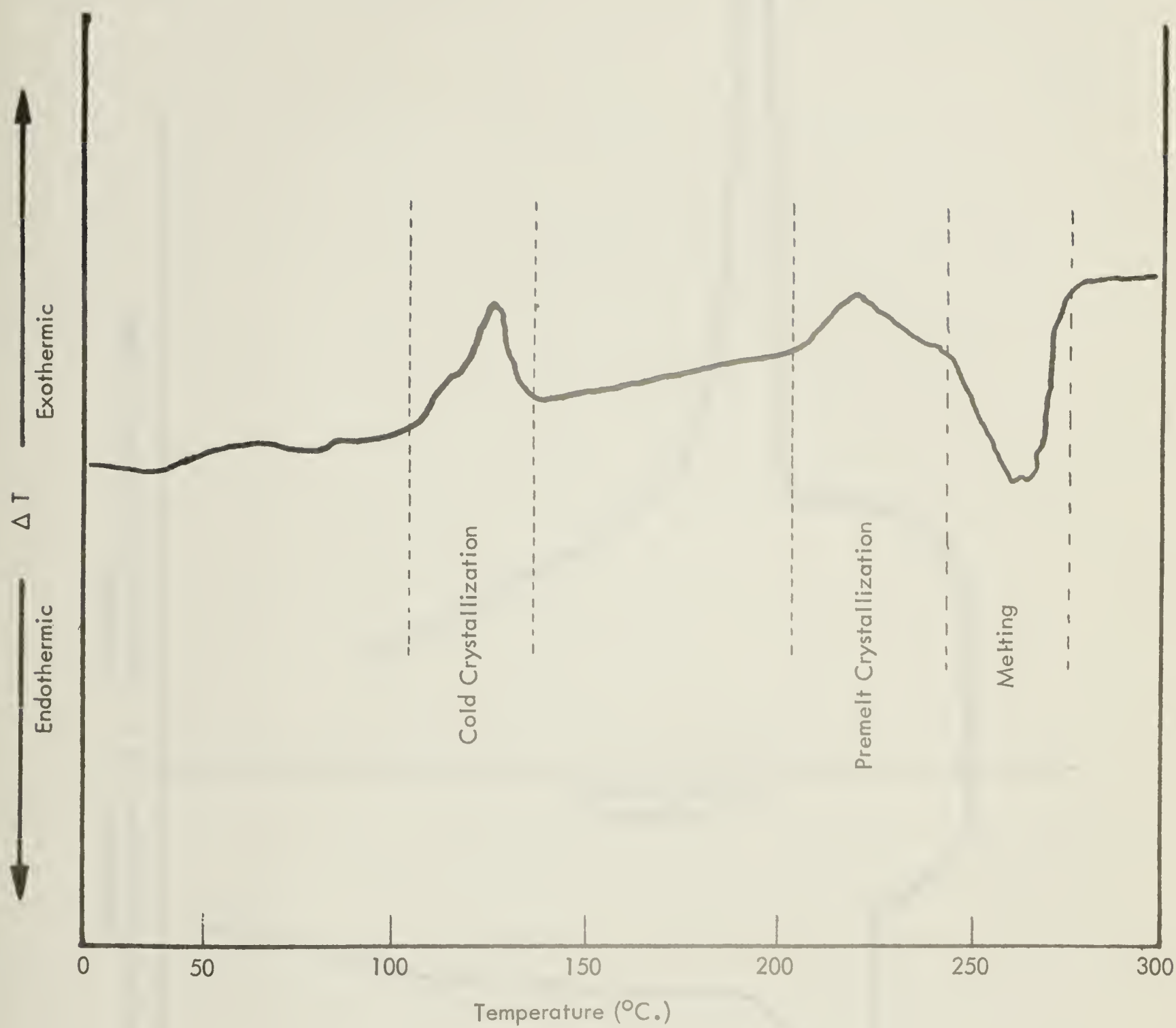
Cold crystallization appears as a bump on the thermogram and does not look at all like the peaks described to date. This is due to the fact that only a small portion of the polymer crystallizes. Chain motion in the amorphous polymer is very slow so only those chain segments which are very close to the proper alignment initially are able to crystallize. Thus the enthalpic effect is very small and the changes are quite gradual.

The cold crystallization peak is most often observed during heating of the block. Thus the heat given off by the crystallization places further heat into the block which must be absorbed by the sample and the reference, causing the bump or peak on the thermogram.

Figures 7 and 8 illustrate the thermograms of polymers undergoing cold crystallization, premelt crystallization and crystallization from the melt.

2. Data which can be Obtained from the Thermogram of a First Order Transition

Data such as the temperature at which the last crystallites melt (T_m), the temperature at which the first crystallites form (T_c), the enthalpy of melting, the



THERMOGRAM SHOWING FIRST ORDER TRANSITIONS
OF POLYETHYLENE TEREPHTHALATE

FIGURE 7

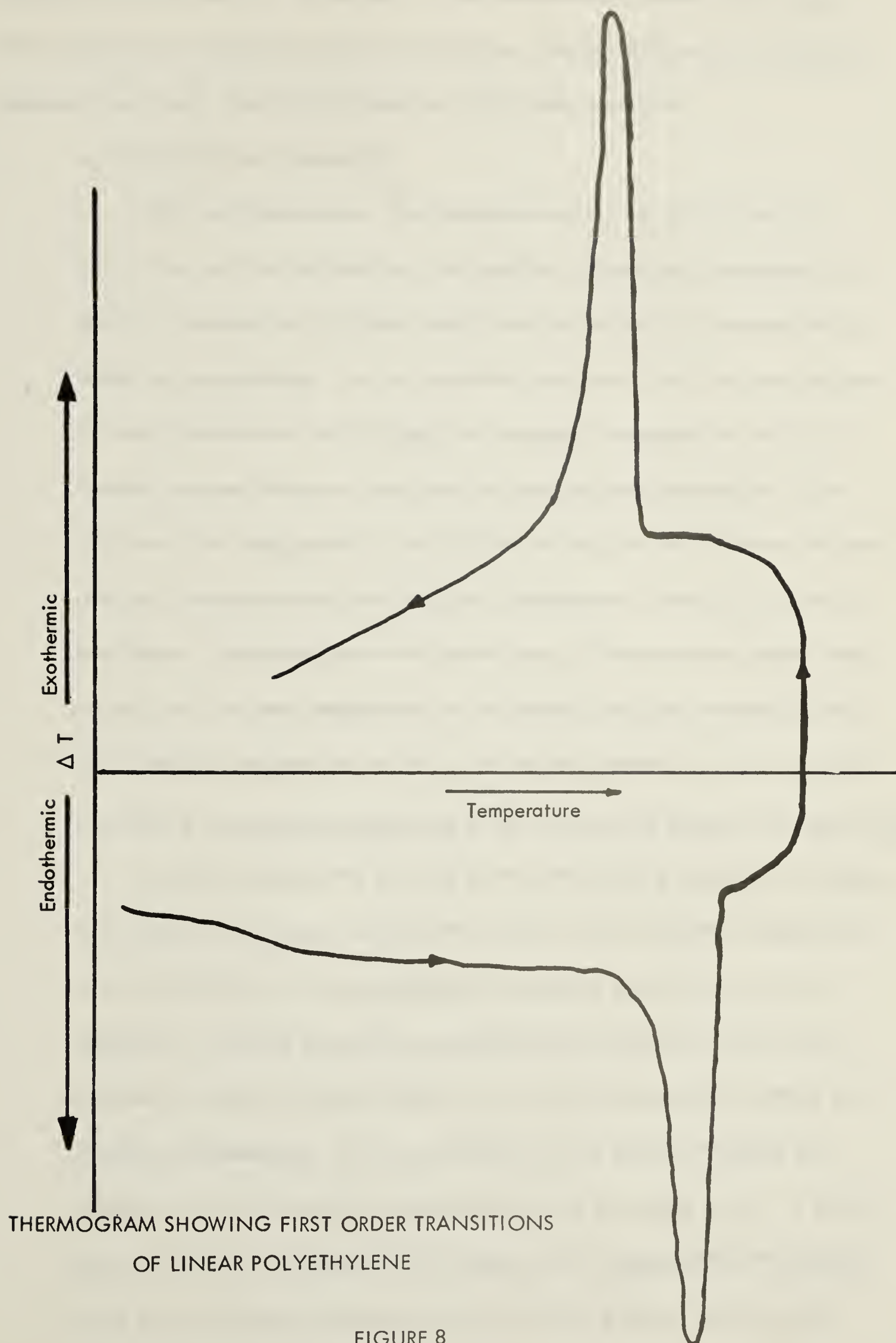


FIGURE 8

enthalpy of crystallization, the percent crystalline material present in the sample, the crystallite size distribution and crystallization rates can be found, with different degrees of accuracy, from the thermograms of first order transitions.

a. The Transition Temperature

The peak temperature, the temperature at the top of the peak just before the return to the baseline, the baseline intersection temperature and points in between have all been used by various authors as a measure of the transition temperatures. As was explained previously, T_m is located between the peak temperature and the baseline intersection temperature while T_c is located between the break from base line and the peak temperature. The location of the exact point is very difficult to find but the difference between the peak temperature and the "baseline" temperature is usually only one or two degrees, depending upon the heating rate. Therefore most authors have agreed upon the peak temperature as the melting transition temperature and the "baseline" temperature as the crystallization temperature. Conventionally the melting is assumed to begin when a 5% rise from the baseline has been observed.

In order to obtain the true end point of the melting transition, Wunderlich (103) set up a master curve for the return of the differential temperature to zero differential. This was obtained by placing a small heater into the sample cell, heating the cell to a predetermined temperature and allowing the heat to decay until zero differential is obtained between the sample and reference temperatures. This was carried out for a number of sample cell temperatures and the results superimposed to give the master curve. A thermogram could then be compared to this master curve, assuming that the heating up of the cell follows the same curve as the cooling down, and the point

where the thermogram peak and the master curve coincide is the end point of the transition. Although this method does not take into consideration the fact that the thermal properties of the unit change when a polymer is placed in the cell, the results compare well with those obtained by other methods. This is probably due to the rapid return to zero differential of the system after a phase change rather than to the use of the master curve.

b. The Heat of Fusion

Values of ΔH for the transition may be quite accurately obtained from the area under the peak. The equipment is first calibrated using a sample of known enthalpy change for the given transition. The peak area for the unknown transition is then compared to this standard. Benzoic acid is often used in polymer work because its melting temperature is in the range of most polymer T_m 's. Inoue (42) used this technique to obtain the heats of crystallization of a number of polyamides and **polyolefins**. Attempts to correlate ΔH and the peak heights have also been tried (44, 107), but these have not been as successful as the area correlations. This is partly due to irregularities in the baseline and the peak shape.

Another method of determining ΔH , which is used in calorimetry but does not appear to have been used in DTA, is the use of a watt hour meter. The meter measures the electrical energy used over the transition range, as compared to that used over a comparable temperature range when no transition occurs. However, this is another piece of equipment which must be calibrated and kept in repair. The peak area technique seems to be sufficiently accurate and does not impose additional problems.

c. The Percentage of Crystalline Material in Polymer

Ke (45) modified the peak area technique to obtain the fraction of crystalline material present in polyolefins. Using the ΔH of benzoic acid to calibrate the equipment, he measured the enthalpy change of dotriacontane (a low molecular weight hydrocarbon polymer). (The results agreed well with those obtained by calorimetry.) This value was assumed to be the same as that of a perfectly crystallized sample of polyethylene, and the crystallinities of other polyethylenes could then be determined by the ratios of the peak areas. The fraction of crystallinity is assumed to be equal to the ratio of the enthalpy change for the semi-crystalline sample, to that of a perfectly crystalline one. A value for the fraction of crystallizable units (X_a), which is often interchanged with the crystallinity, may be obtained by using the classical Flory equation (25):

$$1/T_m^0 - 1/T_m = (R/\Delta H) \ln X_a \dots\dots\dots 11$$

where T_m^0 is the melting point of the pure crystal, R is the gas constant and ΔH is the enthalpy change due to melting of the semi-crystalline sample.

The T_m of dotriacontane can be used for T_m^0 as was done by Ke (45), or the technique established by Holden could be used. Holden (38) ran a series of tests on the same polymer, annealing it at various temperatures above T_m , quenching and then running a DTA melting point determination on each one. He found that a plot of T_m v.s. the annealing temperature showed a rapid rise with increasing annealing temperature and then a levelling off of the T_m values. This steady T_m value was accepted as T_m^0 .

d. The Crystallite Size Distribution

If it is assumed that the peak on the thermogram is a result of only the differences in the crystallite size and order, the distribution of these properties with temperature can also be determined from the thermogram. Starting at the conventional point of melt initiation, the peak is divided into equal temperature increments. The percentage area of each segment gives the percent of crystallites of that particular size and order present in the polymer. This is, of course, only a comparative technique and does not give values of the size or order of the crystallites.

The above techniques can also be applied to crystallization from the melt. The peak area standard would be the area of the peak for the crystallization of benzoic acid or some similar compound. There does not appear to have been any work done in this area, and a value of T_c^0 , the crystallization temperature of a perfect crystal, is not known. Possibly the T_c for a compound like dotriacontane could be used.

e. Crystallization Rates

Crystallization rates may be obtained using a DTA apparatus equipped with a linear gradient furnace or some other means by which the cells may be kept at a constant temperature over a set time interval(20). The thermogram for a sample which has been cooled from the melt to a given temperature, held for a certain length of time and cooled quickly to room temperature is compared to that of a sample which has been quenched from the melt to room temperature. The ratios of the melting peak areas gives a value for the increase of crystallinity due to crystallization at the given temperature for the

given time. If the crystallinity of the quenched sample could be assumed to be zero, the crystallization per unit time could be found for a series of temperatures to give a crystallization rate profile with respect to temperature. But the crystallinity of the quenched sample cannot be zero, thus this factor must be taken into account when determining the crystallization rate at each temperature.

3. Factors Affecting the Data Obtained from the Thermogram

Factors usually affect T_m and T_c in the same way, i.e. those factors which tend to increase T_m also increase T_c and those which lower T_m also lower T_c . Factors which improve the packing of the molecules in a crystal, such as annealing, orienting or cross linking, increase the transition temperatures, while factors such as branching, diluents and co-polymers, which reduce the order of the packing, also reduce the transition temperatures. The transition temperature of a copolymer is linearly dependent upon the amounts and transition temperatures of the comonomers, all other factors being equal.

A review by Ke (49) of some of the factors affecting the DTA first order transitions in polymers showed that the thermal history of the sample affects its melting point through its effect on the crystal size and order. Annealing yields smaller, more ordered crystals than a quenching and yields a high T_m and a sharper DTA peak. Ke also noted that the molecular weight and molecular weight distribution affect T_m through their effect on the crystallite structure. A higher molecular weight increases the order of the crystallites and thus raises T_m . Schwenker and Zuccarello (82) noted that drawn fibres showed slightly higher transition temperatures

than undrawn ones due to their higher degree of crystallization and/or orientation.

Work has also been performed on the effect of thermal history (13, 20, 38, 39, 40, 42, 45, 48, 49, 50, 81, 82), molecular weight (42, 49), branching (48, 50), copolymers (45, 48, 50, 52) and diluents (46) on the first order transition temperatures as examined by DTA.

Holden (38) points out that the calibration of the peak area for enthalpy measurements entails uncontrolled variations of the packing of the samples due to textural differences between the standard and the polymer samples. This he illustrates using the equation developed by Boersma (5):

$$A = Kq/(P\lambda + m\lambda_s) \dots\dots\dots 12$$

where A is the peak area, K is a constant, P is the packing coefficient (which is dependent upon the texture and particle size of the material), λ is the thermal conductivity of the sample. The terms $m\lambda_s$ and $P\lambda$ represent the heat transferred through the thermocouple leads and that conducted by the sample, respectively. Uncontrollable variations in k can be circumvented by using massive thermocouple leads so that more heat is conducted into the cell through these leads. This, however, entails a loss in the sensitivity and resolution of the apparatus.

4. DTA Studies of Polymeric First Order Transitions

DTA studies of the first order transitions of polyethylene (35, 38, 41, 45, 46, 48, 49, 66, 91, 107, 109), polypropylene (20, 32, 41, 45, 48, 66, 82, 91), polyamides (41, 52, 82,), polyvinyls (35, 65, 72), polyesters (2, 50, 81, 82, 83), polybutene-1 (39, 40), polyurethanes (66, 85), PTFE and PCTFE (51, 82, 87, 94), and polycarbonates (67, 74) have been carried out, mainly from an analytical point

of view. In some of these works, however, the polymer was of secondary importance to the transition itself. Wunderlich (107) compared the crystal structure of melt crystallized and solution crystallized polyethylene, and Holden (38) determined that due to different thermal histories, two types of crystals analogous to the types found by Wunderlich occurred in melt crystallized polyethylene. Inoue (42) and Donald et al. (20) were also concerned primarily with the kinetics and thermodynamics of crystallization. Stone (87) was concerned chiefly with the effect of atmosphere and pressure on the transitions while Strella (91) was mainly concerned with heat transfer in a DTA cell during the melting transition.

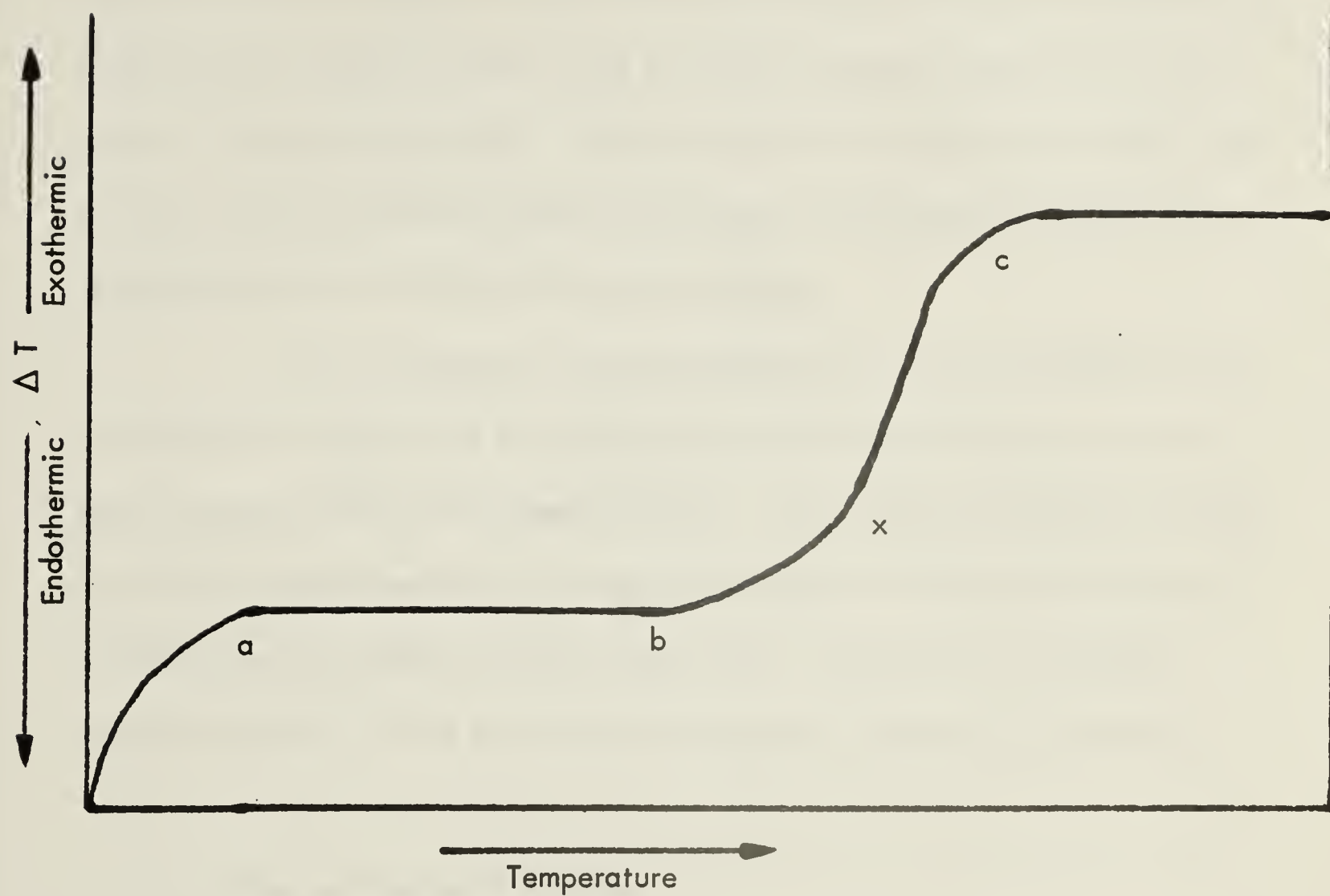
B. Second Order Transitions

As the applications of DTA to the measurement of order-disorder transitions are very limited (only one article has appeared in the literature (51)) due to lack of sensitivity of the instrument, only the glass transition will be discussed in this section.

1. The Thermogram for The Glass Transition.

The thermogram of a glass transition is the result of a temperature differential which develops due to a change in the thermal diffusivity, k , of the polymer. The change in k is quite small and thus the temperature change is slight. Therefore quite large samples (50 to 100 milligrams) are used to make the thermogram large enough to be meaningful. This allows the assumption that the sample and reference are in the form of infinite cylinders to be made.

Figure 9 shows an ideal thermogram. The rise from zero temperature differential between the reference and the sample, to a steady state differential, is shown at "a". At "b" the decrease in k is initiated in the outer annular layer of the sample, thus reducing the heat flow into the center of the sample where the thermocouple is located. This causes the temperature difference between the reference and the sample to increase. The change in temperature differential is indicated by a rise on the thermogram. This process continues as more and more of the sample changes its k value, until at some point "x" between "b" and "c", the entire polymer has reached the new k value. The section of the thermogram between "x" and "c" is the return of the system to steady state. Because of the small change in differential temperature on the thermogram, the mid point between "b" and "c" is usually assumed to be the point of inflection "x", and is thus taken



THERMOGRAM OF TYPICAL SECOND ORDER TRANSITION

FIGURE 9

as the location of the glass transition temperature on the thermogram.

As this is a transition of the amorphous phase, there is no crystallite size distribution mechanism to consider. However, a competing factor in this analysis is that the change in k may not be a sharp step occurring at one temperature, but may be an S shaped function, much as the glass transition appears to be, occurring over a range of temperatures. Literature data (34, 61) indicates the latter type of curve, but this could be caused by transfer lags in the measuring system similar to those described for the DTA of the glass transition.

The ΔT change for the glass transition curve on a thermogram is only 5 to 10% of the change for a first order peak. For this reason very little work has been attempted on DTA of the glass transition. In any early works (53,20) covering this area, the experimental error was high and the effect of heating rate was seen to be within the experimental error and was ignored. The fact that the inflection temperature (x) was not the true transition temperature was not even considered.

2. Data Obtained from the Thermogram

The thermogram described assumes that the X axis thermocouple is located in the block and therefore the temperature recorded on the X axis at point "x" is the surface temperature of the sample when the center is at the transition temperature. The actual glass transition temperature should be point "b", but this is impossible to measure consistently due to deviations in the baseline. The subject of determining the true transition point from a thermogram of the glass transition will be dealt with in a later section.

There are no latent heat effects during a glass transition so that the main thermodynamic property, which is obtainable from the thermogram, is the specific

heat of the polymer. Wunderlich and Bodily (106) explain that specific heat values may be obtained using the equation:

$$C_s \approx D \Delta T + K$$

where D and K are empirical constants. K represents the value of ΔT at steady state in the temperature range below T_g , while D must be determined by comparisons of the increase in ΔT in going from the glassy state to the amorphous state with calorimetrically measured specific heat values.

3. Factors Affecting the Data Obtained from the Thermogram.

External factors and intermolecular variations affect the transition temperature of a glass transition. This can be seen by examining the hole or free volume molecular model. Factors such as cross linking, external pressure, high polarity and high molecular weight tend to reduce the free volume and thus increase the T_g value. On the other hand, diluents, branching, and co-polymers will increase the free volume and decrease the T_g value. These factors will be examined individually for their effect on the glass transition temperature.

a. Molecular Weight

Chain ends are the part of the molecule which cause the greatest increase in free volume when the chain begins to move. They tend to lash and flail around forcing the molecules apart. When the molecular weight is increased, the percentage of chain ends in a given volume of polymer is reduced and the T_g value is raised. Fox and Loshaek (28) developed the classical theory for the dependence of the T_g value on molecular weight (M):

$$T_g = T_g^0 - K/M \dots\dots\dots 14$$

where T_g^0 is the glass transition temperature for a polymer of infinite molecular weight and K is a constant based on the change in specific volume of the polymer caused by the transition. Billmeyer (4), Beevers and White (3) and Eisenberg (23) have expanded or modified this theory.

b. Cross Linking

Cross links bind the polymer molecules together and hinder molecular motion. Thus an increase in the number of cross links will increase the T_g value. Fox and Loshaek expanded the theory given above to also include the effect of cross linking. For high M and low c (concentration of cross links):

$$T_g = T_g^0 - K/M + Kc \dots\dots 15$$

Very polar groups, such as the CN group in polyacrylonitrile or the CHCl group in polyvinyl chloride, may also increase molecular packing and act as weak cross links.

c. Crystallinity

There are two theories on the effect of crystallinity on the glass transition temperature. On the one hand, the crystallites could act as cross links joining the molecules together and raising the T_g values (see 14,41,55), on the other, they could increase the number of chain ends per given volume thus lowering the T_g value (see 3, 41, 80). If more than one molecule occurs in one crystallite, the former would hold, if only a portion of the molecule was crystallized the latter would be the case.

d. Stereoregularity

Closely related to the crystallinity was the stereoregularity of the polymer, i.e. the crystallinity depends in part upon the stereoregularity. Shetter, (84) compared the T_g values of syndiotactic, isotactic and "conventional" (essentially all syndiotactic) polymethyl methacrylate by dilatometry. The values

ranked syndiotactic the highest, the "conventional" and then the isotactic, showing that the syndiotactic form possesses better packing than the isotactic.

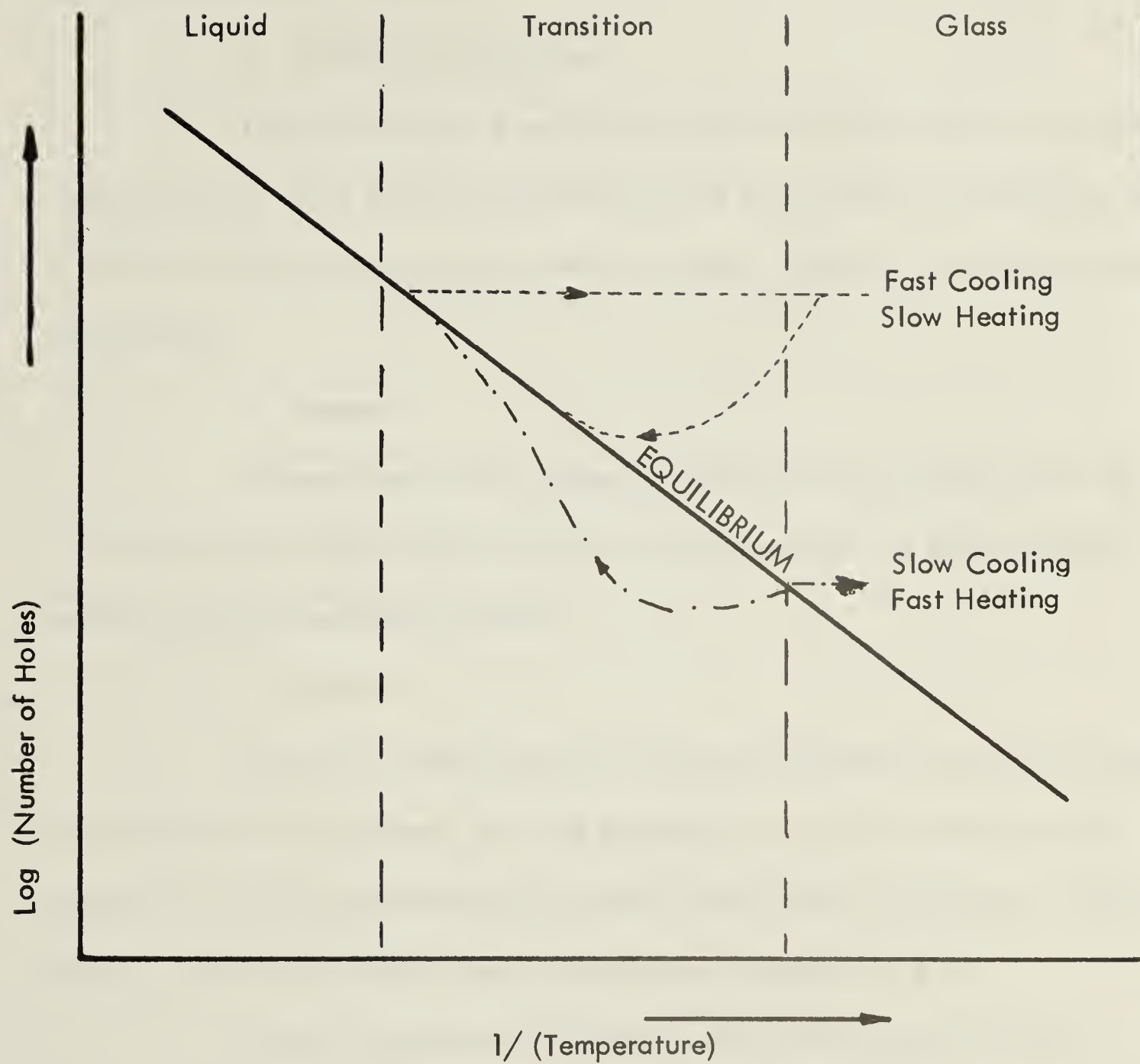
Reding, Walter and Welch (77) studied the effect of polymerization temperature on the glass transition of polyvinyl chloride by measuring the stiffness and the mechanical loss. They found that T_g increases as the polymerization temperature decreases. This they attributed to an increase in the syndiotactic (as opposed to atactic) material present.

e. Branching

Branching has the effect of increasing the chain end concentration, reducing the crystallinity, increasing the free volume and thus decreasing the T_g values. Few analysis have been done on the effect of branching on T_g , but Tanaka (92) found that T_g of branched polyethylene was directly proportional to the concentration of the short branches. He also found that the long branches have no apparent effect on the transition temperature. Willbourn (99) also shows that the T_g values increase as the branch concentration is increased, again for polyethylene using dynamic mechanical analysis.

f. Thermal History

Wunderlich and Bodily (106) investigated the effect of varying the cooling rate on the glass transition. They used what they term Dynamic Differential Thermal Analysis. This consists of controlled cooling as well as the usual controlled heating. The results of such tests on polystyrene were then related to the "hole" theory of Hauri and Ering (36) as modified by Wunderlich (103). This theory is also further improved in his paper. The authors propose a glass transition range and show the effect of heat transfer rate on the hole equilibrium through the transition range as shown in figure 10. However, their results also point out that unless the



EFFECT OF HEAT TRANSFER RATE ON SECOND ORDER TRANSITIONS

FIGURE 10

morphology of the polymer is changed by the change in thermal history, any effects on T_g are only kinetic in nature.

g. Other Chain Properties

Tobolsky (93) lists a few chain properties and their effect on the glass transition point. T_g is directly proportional to the energy barrier to rotation of the C-C bonds in the molecular system, and to the chain stiffness Z , and the chain end concentration.

h. Pressure

External pressure will reduce the free volume and thus increase the T_g values, but the amount of the reduction will depend upon the stiffness of the molecules and the molecular packing.

i. Diluents

Diluents or plasticizers act to increase the free volume of the polymer thus decreasing the T_g values. Fox (26) suggested the use of a copolymer type equation to take into consideration the effect of the diluent on the system. Other theories, modifying this basic idea have also been proposed (3, 8, 89).

A glass concentration has been found for the system polystyrene benzene by Lewis and Tobin (56). They measured the dynamic mechanical properties of the system at constant T and p and varying composition, and obtained curves similar to those obtained by varying T while keeping p and the composition constant.

j. Copolymers

In copolymers the effects of all the previously mentioned factors apply to each of the two different types of polymer chains. Therefore most theoretical work empirically relates the T_g values of the homopolymers to give the T_g value of the copolymer.

4. DTA Studies of Polymeric Second Order Transitions

Very little work has been done on the study of the glass transition by DTA. Polymers which have been studied are: polystyrene (53, 106), polymethyl methacrylate (53, 90), polyvinyl chloride (53), polyacrylonitrile (53), polyethylene terephthalate (83), polypropylene (51) and ethylene-propylene copolymers (108).

Most of these works have been exploratory in nature, primarily to obtain the limits and operating variables of DTA when it is applied to the glass transition. Wunderlich and Bodily (106) however, used DTA to investigate the morphological changes and the mechanisms of these changes during the glass transition. The heat transfer in the DTA apparatus was the main concern of Strella's work (90).

VI. ANALYSIS OF POLYMERS BY DIFFERENTIAL THERMAL ANALYSIS

The use of DTA for polymer analysis to find such items as the amount of each comonomer in a copolymer, the amount of plasticizer in a polymer, the composition of a polymer mixture or the identity of an unknown polymer, is one of the more useful aspects of this tool. However, as so many factors affect the transition temperatures of polymers, a certain amount of previous knowledge or intuition must be applied to the results of a differential thermal analysis in order to interpret them. Also DTA apparatuses vary so much that literature thermograms are only of qualitative interest. Nevertheless, each polymer system does have its own transition temperatures and peak shapes so that if a file of thermograms of known polymer systems were made up, DTA could be a very effective analytical tool. Values of the glass transition temperatures for a number of polymers have been tabulated in Appendix 1 for use as a guide for the thermal analysis of polymer systems. An excellent review of melt transition data is given by Mandelkern (60).

The literature on quantitative or qualitative analysis of polymer systems by DTA is quite limited, probably because the bulk of the emphasis to date has been either to find the limitations of the DTA technique, or to use DTA as a tool in investigating polymer morphology. Characterizations by DTA have been carried out on systems of polyesters (50, 70, 81), polyurethanes (85), polyolefins (45) and polyamides (52).

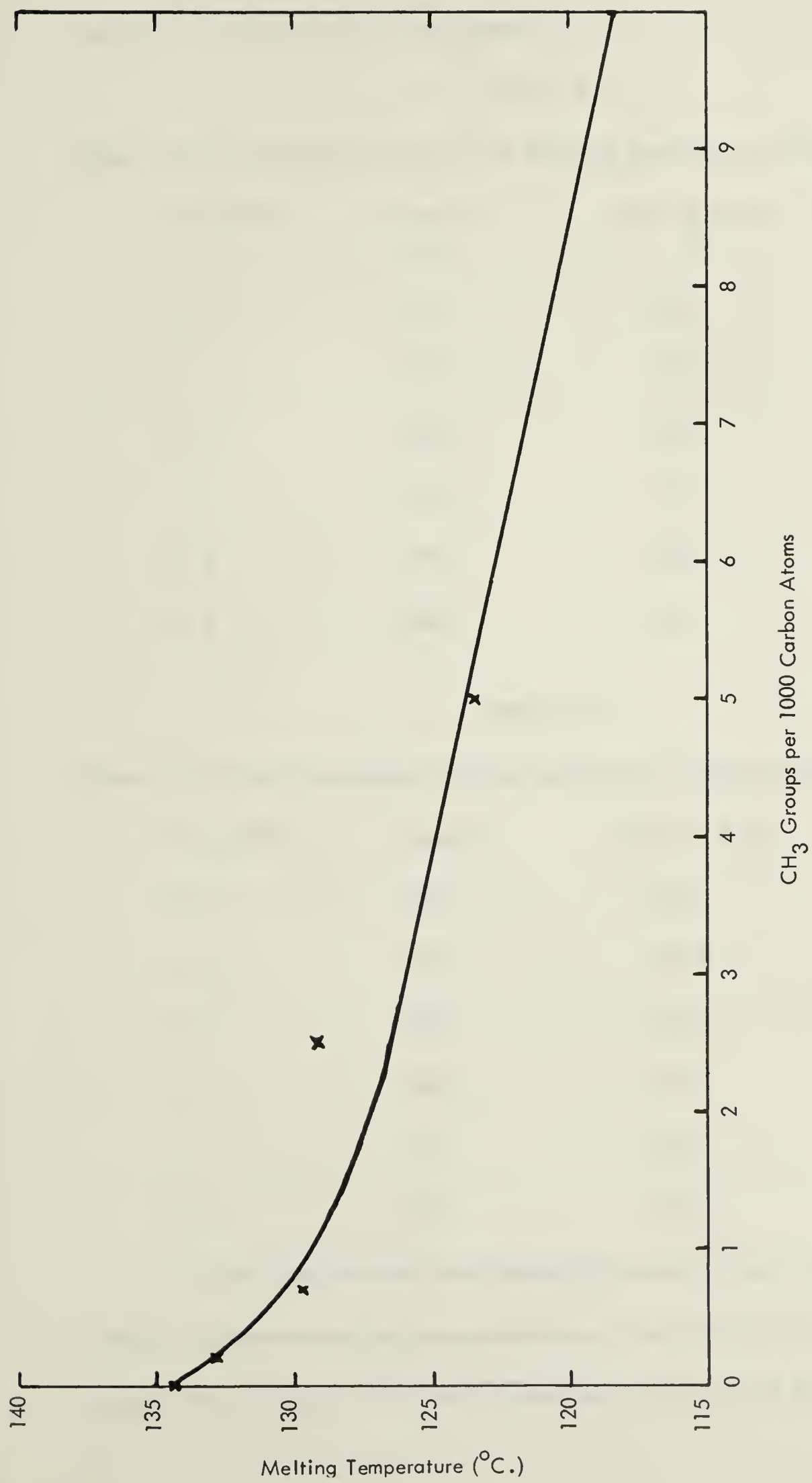
The most important advantage DTA has over other methods of analysis is the rapidity of the tests. However, a complete thermogram, covering some or all of the factors: glass transition, cold crystallization, oxidation, melting, and decomposition

is still quite time consuming because of the large temperature range encompassed. Specialization on one of these phenomena would appear to allow for a rapid determination of the components of a system, Concentration on a single feature is most useful for analysis of a two component system (copolymers or polymer diluent) when only the quantities are unknown, while the complete thermogram is better suited for identification of a single polymer or of polymers making up a copolymer. The two approaches are often necessary in an analysis to give a more complete body of data for interpretation.

The individual changes which make up a complete thermogram have been described in previous sections. The use of the first and second order transitions as analytical tools will be examined here.

1. Analysis of Polymer Systems Using the First Order Transitions

A few analyses of copolymers by DTA, showing the effect of the copolymer units on the melting point, are described in the literature. Ke examined the DTA thermograms of polyethylene-terephthalate (50), polyamides (52), and polyolefins. (45,48) and showed a melting point depression due to the less crystalline copolymer units. However, he did not examine the results from an analytic point of view. His works were primarily to show the types of data produced using DTA. Wunderlich and Poland (109) showed the effect on the melting point of various concentrations of CO and CHCH₃ copolymer units in high density, linear polyethylene. The CO copolymers were not a consistent series, so the results did not show any definite trend. However, the ethylene-propylene copolymer series was consistent, and the effect of the copolymer units on the melting point can be clearly seen. (See table



EFFECT OF SHORT CHAIN BRANCHING ON MELTING TEMPERATURE

FIGURE 11

A and B for the results of these tests, and figure 11 for the relationship of T_m to the amount of propylene in the copolymer.)

TABLE A

Effect of CO Copolymer Units on the Melting Temperature of Polyethylene

CO/100C	Density g/cc	Melting Temp. °C	%Crystallinity
0.0	.977	134.4	99.5
1.7	.919	99.0	90
3.0	.939	103.2	91
5.2	.942	91.7	89
9.0	.991	96.8	92
13.2	1.022	90.8	92

TABLE B

Effect of CHCH₃ Copolymer Units on the Melting Temperature of Polyethylene

CH ₃ /100C	Density	Melting Temp.	%Crystallinity
0.0	.977	134.4	99.5
0.2	.955	132.8	99
0.7	.942	129.6	98.2
2.5	.948	129.3	98
5.0	.912	123.5	97.6
10.0	.885	118.5	95

Ke (46) also showed the effects of diluents such as chloronaphthalene, tetralin, phenanthrene and dotriacontane on the melting point of both high and low density polyethylene. His results correlated well with the Flory equation (25);

(a modification of equation 11)

$$1/T_m - 1/T_m^0 = (R/\Delta H)(V_2/V_1)(\phi_1 - X_1\phi_1^2) \dots\dots\dots 20$$

where in this case T_m is the melting point of the system, T_m^0 is the melting point of the pure (perfectly crystalline) polymer, V_2/V_1 is the ratio of the molar volume of the polymer to the molar volume of the diluent, ϕ_1 is the volume fraction of diluent present in the system and X_1 is the "thermodynamic interaction parameter".

($X_1 = BV_1/RT$ where B is the "interaction energy density" of the polymer). Only concentrated polymer solutions were examined, due to difficulties in obtaining reproducible results for the dilute solutions.

From the point of view of a rapid analytic procedure, this technique has one draw back. Because the crystalline structure, and thus the melting temperature, of the polymer is very dependent upon the thermal history of the resin, the samples must be heated to above the melt temperature and then cooled at a uniform rate to ensure the consistency of the morphological state of the various polymers tested. This means also that careful records of the thermal history of the polymers for any thermograms, which are to be kept on file for comparison purposes, must be kept and that the polymers compared to them must have the same thermal history.

Therefore it was decided that the use of the glass transition for predicting the compositions of polymer systems should be investigated.

B, Analysis of Polymer Systems Using the Second Order Transitions

The glass transition temperature has been used in copolymer analysis by a number of authors (see the data in Appendix 1), but no mention has been found in the literature for the application of DTA to this technique. In order to investigate

the usefulness of DTA in this area of study the pertinent theories were first examined.

a. Theories of the Glass Transition of Co-polymers

The following symbols will be used throughout this section:

W_i = weight of the homopolymer unit i

M_i = molecular weight of the homopolymer unit i

Tg_i = the glass transition temperature of the homopolymer unit i

C_i = the concentration (mole fraction) of the homopolymer unit i

Gibbs and DiMarzio, building upon their statistical thermodynamic description of the glass transition temperature (29,30), developed a rigorous equation for the glass transition temperature of a copolymer (31):

$$(W_1 C_1 / M_1)(Tg - Tg_1) + (W_2 C_2 / M_2)(Tg - Tg_2) = 0 \dots\dots\dots 21$$

This theory breaks down, however, at the points of 12 linkages, but this effect has been proven slight.

Equation 21 is similar to the general equation Wood (102) bases his description of the glass transition of copolymers on:

$$(A_1 C_1 (Tg - Tg_1) + A_2 C_2 (Tg - Tg_2) = 0 \dots\dots\dots 22$$

where A is an empirical constant. This equation, Woods states, can be arrived at by a number of theoretical approaches, each giving a slightly different significance to the constants A .

If A_1/A_2 is set equal to k , rearranging 22 yields the equation developed by Gordon and Taylor (33):

$$Tg = (Tg_1 + (kTg_2 - Tg_1)C_2)/(1 - (1-k)C_2) \dots\dots\dots 23$$

where k is always less than or equal to one.

Mandelkern, Martin and Quinn (61) defined $R = kTg_1/Tg_2$ to obtain:

$$1/Tg = (1/(C_1 + RC_2))(C_1/Tg_1 + (RC_2/Tg_2)) \dots\dots\dots 24$$

which reduces to the equation developed by Fox (26) for $R = 1$:

$$1/T_g = C_1/T_{g1} + C_2/T_{g2} \dots\dots\dots 25$$

The significance of the A_i values in the above equations are given by the various authors in terms of volume temperature coefficients.

Gibbs and Gordon and Taylor assumed an ideal co-polymer, with the partial specific volumes of the components constant and equal to the specific volumes of the homopolymers, and with constant volume temperature coefficients in the glassy and the rubbery states. Thus they obtained values of A as the difference between these volume temperature coefficients for the two regions. Mandelkern et.al. made the same assumptions, plus the assumption that the specific volume was the sum of a free and an occupied volume, each with its own VT coefficient ($C(VT)$) to obtain values of A_i equal to:

$$A_i = C(VT)_{1r} - fC(VT)_{1r} + C(VT)' \dots\dots\dots 26$$

where f is the volume fraction of the free volume, and the superscript ' refers to the occupied volume fraction. The authors state that experimental data on these quantities are very inaccurate and recommend the use of the factor R .

Tobolsky (93) gives the following empirical equation for copolymers of styrene and butadiene:

$$T_g = C_1 T_{g1} + C_2 T_{g2} \dots\dots\dots 27$$

Equation 27 has been modified by Ellerstein (24) for the interaction of the two comonomer segments:

$$T_g = c_1 T_{g1} + c_2 T_{g2} + 2c_1 c_2 T_{g12} \dots\dots\dots 28$$

where T_{g12} is the T_g of a 50-50 co-polymer of 1 and 2 or approximately equal to

$(T_{g1}T_{g2})^{1/2}$. Ellerstein does not put any stipulations on the polymer systems this equation is applicable to.

Hayes (34a) gives the empirical equation:

$$T_g = \frac{H_c + 25n}{0.5nR} \dots\dots\dots 29$$

for most polymer systems. For copolymer H_c is the molar cohesive energy of the copolymer ($H_c = x_1HC_1 + x_2HC_2$), R is the gas constant and n is "a number analogous to the degrees of freedom in expressions of kinetic energy." The author gives values of H_c and n for a number of polymers and also a list of rules for calculating n .

Most of these theories have been checked with experimental data. Wood used literature data on the systems styrene-butadiene, vinylidene fluoride and chlorotrifluoroethylene, and butyl acrylate and methyl methacrylate, using modified forms of equation 23. Gibbs and DiMarzio checked their theory with literature data for 10 copolymer groups and obtained deviations of from -12.9 to + 9.8 %. Mandelkern, Martin and Quinn measured the T_g 's of a polychlorotrifluoroethylene polyvinyl fluoride system and five other co-polymers by dilatometry to check Fox's equation, (equation 25) and found that in order for this equation to be obeyed, the required T_g of the polyvinyl fluoride would have to be about 15°C. below that observed. Howard (41) investigated the system polyacrylonitrile (PAN) and polyvinyl acetate (PVA) by dilatometry and, excepting a crystalline phenomena at high PAN concentrations, found a good fit with equation 4 from the work of Mandelkern et.al., with R having an empirical value of 2.7.

VII. OTHER USES OF DTA IN THE FIELD OF POLYMER SCIENCE

Any phenomena of polymers which has a heat effect can be measured by DTA to a greater or lesser degree of accuracy. Effects such as oxidation and decomposition play an important role in analysis, while effects such as the heat of reaction are studied for their own worth. Some of these phenomena will now be examined in more detail.

A. OXIDATION

Almost all hydrocarbons, including most polymers, are prone to attack by oxygen at high temperatures. The oxygen combines with the polymer to form compounds, usually of the hydroperoxide types, in an exothermic reaction. Most reactions are characterized by a slow oxidation in which hydroperoxides are formed, and a fast oxidation in which these peroxides break up and autocatalyse the further reaction with oxygen.

Ke (49) used the DTA technique to examine the oxidation of a number of polyethylene samples, and to determine the effects of several antioxidants in impeding the reaction. Rudin, Schreiber and Walden (79) carried out similar tests, and also compared the results with more conventional methods of measuring the oxidation phenomena, with very good agreement. Schwenker and Zuccurello (82) measured the oxidation of various fibres using DTA.

B. DECOMPOSITION

When heated to a high enough temperature, polymers will decompose either by scission or by catalytic depolymerization. In the former case, the bond vibrations

become so great that the bond splits apart and the smaller free radicals produced combine into lower molecular weight compounds. In the latter case, products in the surroundings catalyse the breaking of the bonds in the polymer. These decompositions are associated with an endothermic reaction, which can be measured by DTA. However, this technique has only been used as part of a polymer analysis, not for a study of the decomposition reaction as such. For this latter type of study, thermal gravimetric analysis appears to give better results (weight loss is measured as a function of the temperature). A DTA apparatus with a gas chromatograph attached to the gas outlet from the sample chamber would seem to be ideal for such studies, as this equipment would yield the heat of the decomposition (which could probably be correlated with the weight loss) and the identity of the decomposition products. This is a new technique and the results have not been recorded in the literature, therefore a quantitative measure of its effectiveness is not available.

C. CHEMICAL REACTIONS

Borchard and Daniels (6) have covered the general approach in using DTA to investigate the kinetics of solid state chemical reactions. Making the assumptions that:

- i. the temperatures of the two cells are the same initially
- ii. heat transfer is by conduction only
- iii. the heat transfer coefficients of the two cells are the same
- iv. the heat capacities of the sample and reference materials are the same (the sample is greatly diluted by reference material so this assumption is quite good)

- v. the enthalpy change of the reaction can be given as a linear function of the area under the peak on the thermogram (A)

the authors are able to develop equations for calculating:

- i. the reaction rate from the slope of the peak to a given point on the thermogram, and its height above the baseline
- ii. the number of moles reacted to temperature T from the area under the peak to temperature T
- iii. the rate constant from the slope and height of the peak and the area under it. In this case the order of the reaction must be known.

This method of determining the above factors was tested on DTA studies of the reaction between dimethylaniline and ethyl iodide, and the decomposition of benzene diazonium, and found to be very accurate and fast.

Polymerization, being a chemical reaction, has definite heat effects which can be related to kinetics of the reaction. DTA has been used to give both the temperatures of initiation and completion of the reaction, and the heats of polymerization for polymerization of polyesters by Murphy (68, 69) and Clampitt, German and Galli (11, 12). The two techniques are both quite different, but both appear to give quite good results. Murphy used samples with different degrees of cure and ran conventional DTA's on them, obtaining an analysis of the components present in the partially cured resin. Clampitt et.al. placed the reactants into the sample cell of the DTA apparatus and heated the cell conventionally. The thermograms obtained gave the temperature range of the reaction and the enthalpy change accompanying it.

All of these works show definite advantages for DTA in a polymerization

reaction (the heat effects are more pronounced) than are other physical properties. Unfortunately most polymerization reactions are highly sensitive to contaminants so that the conventional DTA apparatus could not be used to analyse them. The modifications necessary to make the apparatus applicable would be quite extensive in most cases, which would probably make this technique undesirable.

D. APPLICATIONS OF DTA IN INDUSTRY

Most of the large polymer producers in Canada now are using some type of differential thermal analysis equipment to assist in many phases of their research into the make-up and properties of polymers. DTA is used for product analysis, effects of additives on the morphology, effects of the chain structural variations on the morphology, control of pretreatment to yield desired properties in the resin, and as a quality control technique. The uses are growing and the equipment is becoming more refined and capable of a greater range of analysis at higher degrees of accuracy.

VIII. EXPERIMENTAL

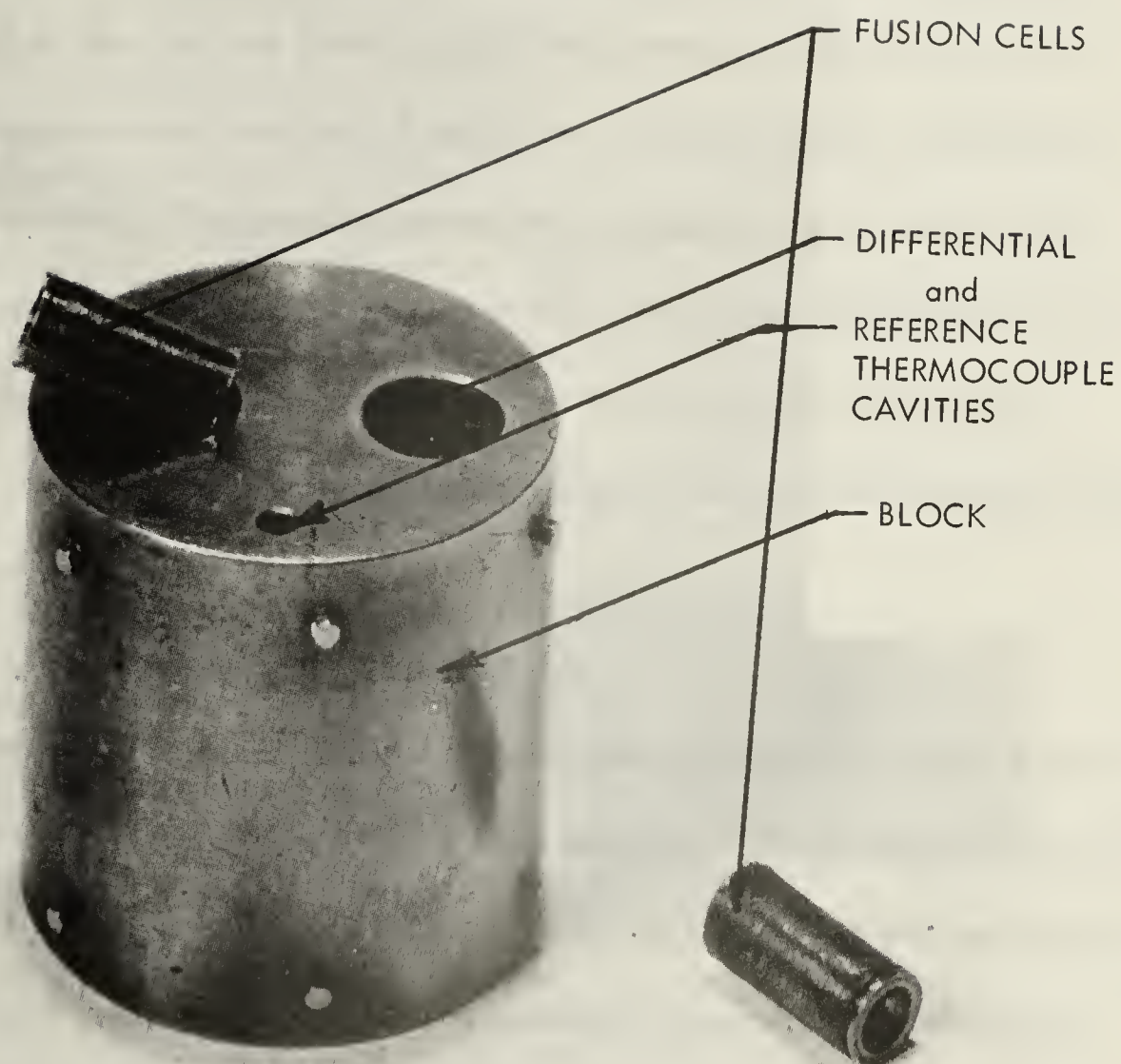
As differential thermal analysis is still a relatively new tool for polymer investigations, this study was initiated as a general investigation of the uses of DTA for measuring various polymer transitions. It was decided to put the emphasis of the investigation on measuring the glass transition temperatures of polymers and to look into the possibilities of analyzing copolymer systems by means of their glass transition temperature. The study of the glass transition measurements pointed out the need for further work on the interpretation of thermograms. This was undertaken with emphasis on the thermograms of the glass transition.

A. Equipment

Studies of the differential thermal analysis of polymers in this work were carried out using an Aminco Thermoanalyser, Model 4-4442, belonging to the Soil Science Department of the Faculty of Agriculture at the University of Alberta. It consisted of the following main components:

a. The Sample Block (figure 12).

Two, one inch diameter by one inch long sample blocks, are provided with the unit, one for dry, powdered material and one for liquids or materials which might melt during the analysis. The cast iron block, used for dry powders, contains two material cavities 0.2 inches in diameter by 0.5 inches long located symmetrically in the top portion of the block. These cavities open out to 0.3 inches in diameter for the bottom half of the block to accommodate the differential thermocouple. A smaller hole, 0.05 inches by 0.5 inches long, is also located in the bottom half of the block on the same diameter as the outside of the material cavities - accommodating



THERMOANALYSER BLOCK
FIGURE 12

the reference or X axis thermocouple. This block temperature is assumed to be the same as the surface temperature of the material cylinders due to the placement of the thermocouples.

For materials which would liquify in the analysis, a stainless steel block, exactly the same as the cast iron block except for the material cavity design, is provided. The material cavities are 0.4 inches in diameter allowing a shoulder at the base of the cavities. The sample and reference materials are enclosed in thin walled stainless steel cups which fit into the cavity and rest on the shoulders. The bottoms of the cups are recessed to accept the two branches of the differential thermocouple. Four very small holes around the cups in the cavities allow gas to be circulated around the samples.

b. The Thermocouple Assembly (Figure 13)

The thermocouple assembly consists of a chromel alumel differential thermocouple and a reference thermocouple of the same material. The differential thermocouple consists of two balanced thermocouples 12 inches long, which are covered by 10 inch by 0.3 inch ceramic insulators. The reference thermocouple is the same as either side of the differential thermocouple and is used without insulation. The insulation on the differential thermocouple serves a threefold purpose: to support the block, to allow a passage for gas from the cells, and to prevent heat transfer between the leads. In the cast iron block the thermocouples protrude into the sample and reference while in the stainless steel block the two cups rest on the ends of the thermocouples. The thermocouples, with the cast iron block on top, can be seen on the left of figure 13.

The differential thermocouple signal is amplified by a low noise chopper input

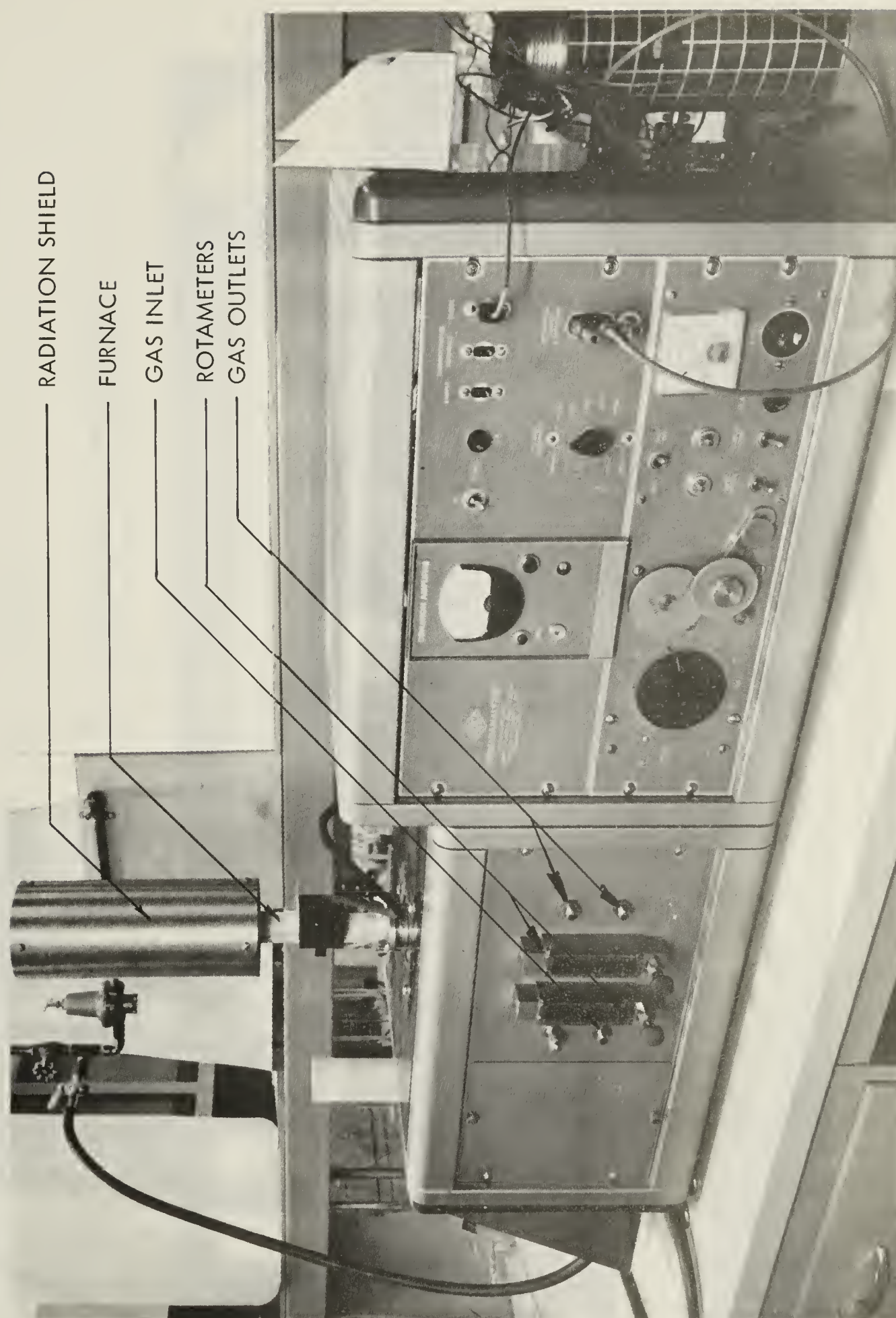
amplifier (on the control panel to the right of figure 13) and fed to the Y axis of the recorder. The unit is wired so that any of the three thermocouples (i.e. the sample, reference and block thermocouples) may be used for the X axis signal. The recorders used in this work were a Speedomax Model R-504-L-221-A and a Moseley Model 2D.

c. The Furnace (Figure 14)

The furnace is based on the design by Lodding and Hammel (59) and consists of heater coils in a porcelain shell fifteen inches long by three inches outside diameter. It fits snugly over the block and thermocouple assembly and bolts onto the stand as shown on the left of figure 14. The furnace is insulated with an aluminum radiation shield, also shown in figure 14. The power supply to the heater is programmed to give a steady heating rate by means of a motor driven gear system, shown on the control panel near the center of figure 14, on a powerstat. Rates of from $1/4^{\circ}\text{C.}$ per minute to 16°C. per minute can be supplied by changing the gears and/or the motor. Two motors are provided to cover the ranges $1/4^{\circ}\text{C.}$ to 2°C. per minute and 2° to 16°C. per minute.

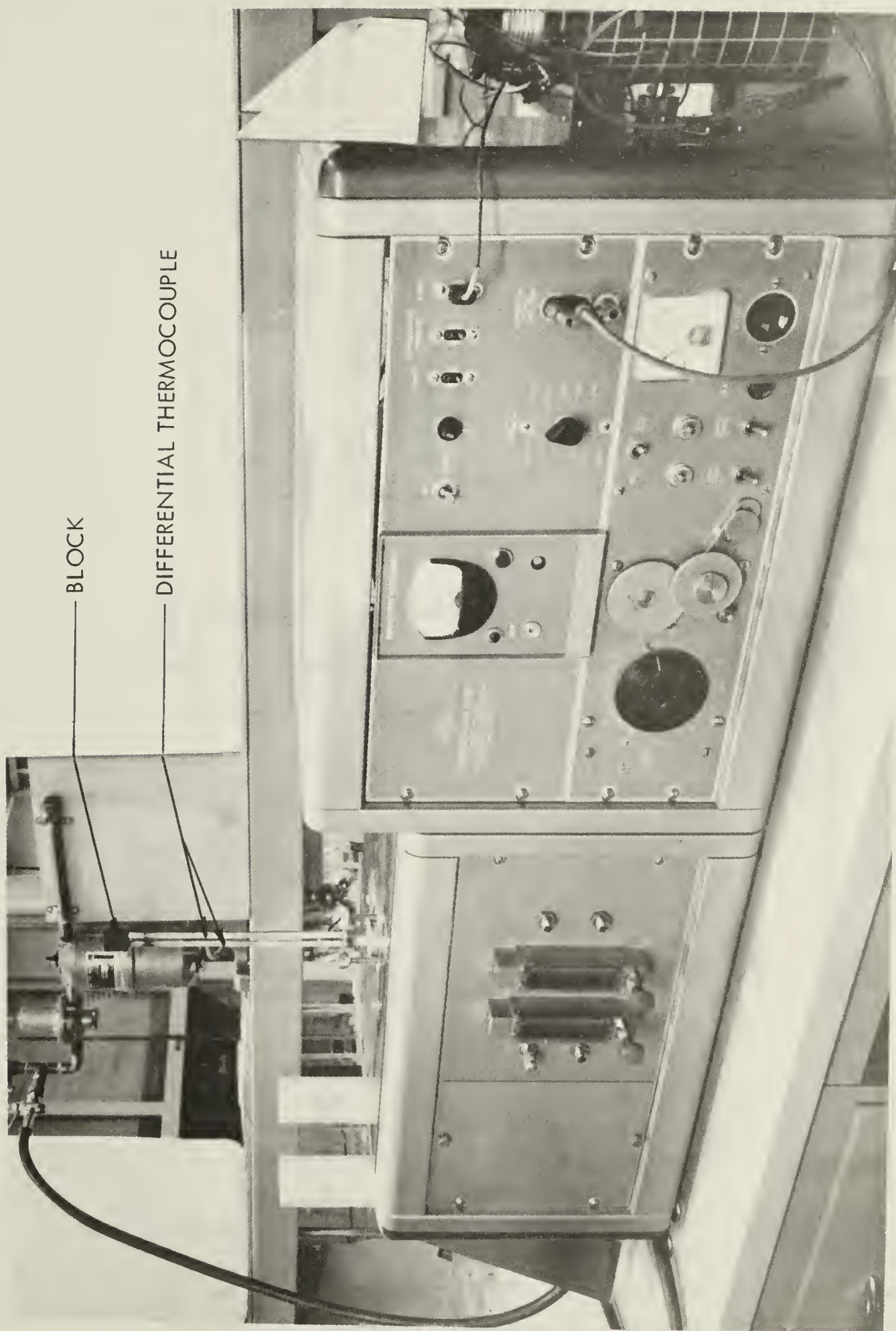
d. The Gas Flow System (figures 13, 14 and 15)

Means of supplying a controlled atmosphere to the cell is provided for the apparatus. The gas from a cylinder flows into the center part of the furnace on the outside of the thermocouple insulation, over the top of the block, through the sample and reference (assuming that they are in the powdered form in the cast iron block), down the insulators on the differential thermocouple, through two rotameters on the bottoms of the two insulators and out to the atmosphere. The flow is shown on figure 15, and the gas inlet, outlets and rotameters can be seen on the left panels in figures 13 and 14. If the stainless steel block and the sample cups are used it is



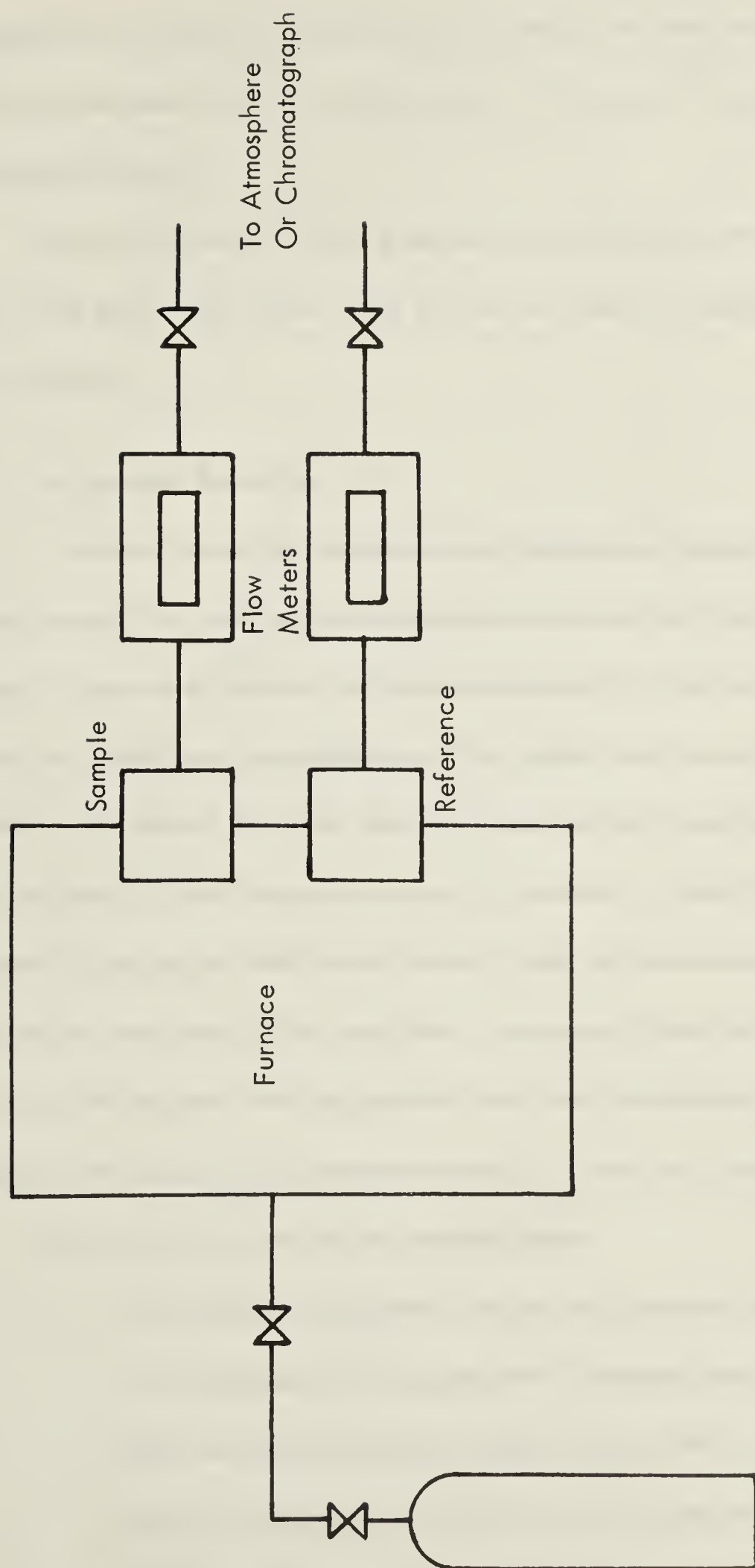
AMINCO THERMOANALYSER

FIGURE 13



AMINCO THERMOANALYSER

FIGURE 14



GAS FLOW SYSTEM OF AMINCO THERMOANALYSER

FIGURE 15

not possible to circulate the gas through the sample and reference, so only their upper surfaces are exposed to the circulating gases. Therefore this unit is usually only used for powdered samples.

The composition of the off gases may be analysed by attaching a gas chromatograph to the sample gas outlet. This can be very useful in degradation and decomposition analyses.

B. The Melting Transition

In order to check the procedures and techniques necessary for the analysis of polymers using DTA, melting point determinations were carried out on two polyethylene samples. These were the same as those samples used by Holden (38) for an analysis of the melting transition of polyethylene. The results were compared to those obtained by Holden. Polymer P is a high density, linear polyethylene ($M_n = 12000$, $M_w = 90000$) while polymer Q is an intermediate density, branched polyethylene (melt index 20, 19.3 methyl groups per 1000 carbon atoms). Both polymers were finely ground when received and were used in this condition. Powdered 60 mesh alumina was used for a reference with polymer P while polymer P was used as reference with polymer Q to investigate the effect of the reference material on the peak temperatures.

Three tests were carried out on these resins.

1. 73 milligrams of polymer P and 80 milligrams of alumina were placed in the stainless steel cups and the Thermoanalyser was assembled. The block was slowly heated to approximately $140^{\circ}\text{C}.$, held at this temperature for 15 minutes and slowly cooled to ambient temperature. The sample was then assumed to be in a homogeneous state for the start of the test. The unit was then heated at one degree per minute to

approximately $140^{\circ}\text{C}.$, held at this temperature for 15 minutes and allowed to cool to ambient temperature at approximately $1/2^{\circ}\text{C}.$ per minute. This constituted one thermogram. The procedure was then repeated to check the reproducibility of the thermograms.

2. 80 milligrams each of polymer P and alumina were prepared for testing as outlined in 1. The unit was then heated at two degrees per minute to around $140^{\circ}\text{C}.$ held for fifteen minutes and allowed to cool to ambient temperature at 1.6 degrees per minute. This procedure was repeated except that the cooling rate was increased to eight degrees per minute. This procedure was then repeated exactly.
3. 65 milligrams of polymers P and Q, being used as sample and reference, were prepared for testing as outlined in 1. The unit was then heated at one degree per minute to around $140^{\circ}\text{C}.$, held for fifteen minutes and allowed to cool to ambient temperature at one half degree per minute. This was repeated only the heating rate was increased to two degrees per minute.

C. The Glass Transition

1. Polystyrene

Three samples of Dow polystyrenes, (330, 475, and 683) and one of Koppers polystyrene were used for glass transition temperature determinations using the Aminco Thermoanalyser. The Dow samples were ground to approximately 60 mesh using a Braun Type UA Pulverizer cooled by mixing the polymer with dry ice before and during grinding. The Koppers sample was already in the powdered state and was used as received. Seventy to eighty milligram samples were used with alumina references

in the cast iron cell. All the samples were heated from ambient temperature at rates of 3.1, 6.3, 9.6 and 12.3 degrees centigrade per minute. All samples were heated to 122°C. and cooled at 8 degrees per minute before testing, in order to reduce the crystallite content of the polymer.

2. Copolymers

a. Samples

Samples of butadiene-styrene, and butadiene-acrylonitrile copolymers used in this work were donated by the Polymer Corporation, Sarnia, Ontario, and the compositions are outlined in table C. These samples were run as received, and also the butadiene-styrene samples were extracted for three days in an ethanol toluene azeotrope solution (prepared according to ASTM specification D-1416-62aT for the analysis of the plasticizer content of butadiene-styrene copolymers) to remove the plasticizers. Table D shows the plasticizer content before and after the extraction.

b. Procedure

It was thought that the composition of the copolymer samples could be obtained by measuring the glass transition temperature of the copolymer and finding the point on a theoretically obtained glass transition temperature v.s. composition curve for that copolymer. This was tested by using the samples mentioned above (compositions known) and various theoretical relationships obtained from the literature. (See section V.)

The glass transition temperatures of these samples were not easy to obtain because all occurred at well below ambient temperatures. The Aminco Thermoanalyser allowed the materials to only be heated so the unit had to be cooled before the

TABLE C

COMPOSITION OF CO-POLYMERS

A. Butadiene-styrene

Sample	Wt. % Styrene	Hydrocarbon Content	Ash %	Soap %	Acid %	Stabalizer %	Emuls. %
Krylene NS	27.6	91.8	.76	.039	5.52	1.25	.63
Krylene 608	46.8	90.5	1.20	.028	5.92	1.25	1.10
Krylene	23.8	90.2	1.03	.001	6.58	1.25	.97
S-630	27.9	91.8	1.16	.101	5.26	1.25	.45

B. Butadiene-acrylonitrile

	Wt. % Acrylonitrile						
Krynac 802	27.6	96.6	.43	--	---	1.3	--
Krynac 803	35.3	96.4	.47	--	---	1.2	--
Krynac 805	39.9	96.3	.43	--	---	1.1	--

TABLE D

DILUENT CONTENT IN STYRENE-BUTADIENE COPOLYMERS

SAMPLE	TOTAL DILUENT CONTENT(WEIGHT %)		STYRENE WT. % After Extraction
	Before Extraction	After Extraction	
Krylene NS	8.2	1.7	29.6
Krylene 608	9.5	3.9	49.6
Krylene	9.8	1.1	26.1
S-630	8.2	1.2	30.0

thermal analysis could be started. A procedure outlined by the staff of Aminco was tried first. This technique consisted of filling the furnace with liquid nitrogen, allowing the system to come to equilibrium, filling the top part of the furnace with glass wool to absorb the liquid nitrogen, placing the furnace over the block, placing an asbestos insulating cover and an aluminum heat shield over the furnace, and again waiting for equilibrium. Liquid air was used in place of the nitrogen suggested. It was found that temperatures of no better than -20°C . could be obtained, and that equilibrium could not be obtained due to heat leaking in from the surroundings. As a greater degree of cooling was necessary the block was also cooled by immersion in liquid air. This created a number of problems with the sample and reference materials. In the powdered state the boiling of the liquid air drove the materials from the cells, and in the fused state the severe cold caused the materials to expand thus sealing off the holes made by the thermocouples. The final solution entailed using the stainless steel block and cups, fusing the materials, (This meant that some material other than the conventional alumina had to be used for the reference. Either polystyrene or one of the other copolymers were used in these tests,) and then quenching in the liquid air.

One further trouble remained throughout the trials. As explained previously (section IV), a steady temperature difference between the sample and reference is necessary to give a straight baseline. This meant that the system must be in dynamic equilibrium. Considering that the change in the temperature difference between the reference and the sample during a glass transition is less than one degree, it can be seen how necessary this steady baseline is in the determination of the glass transition temperature. In the procedure used for the glass transition analysis of the

copolymers, the furnace and the block are seldom at the same temperature at the time of their initial contact, and heat is being gained from the surroundings at all times. These conditions combined to produce a fluctuating baseline and make the interpretation of the thermogram quite difficult. The only apparent way around this problem was to set up a liquid air circulation system through the furnace or the block. This solution was rejected as too costly and troublesome for this work and the problem was 'lived with'.

Fifty to seventy milligram portions of the sample and reference materials were used in each case, and heating rates from 3 to 14 degrees centigrade per minute were tried.

D. Interpretation of the Thermograms

This section is limited to the interpretation of thermograms for second order transitions. Because of the practical difficulties in interpreting thermograms of the glass transition, it was felt that a good theoretical basis was necessary before any interpretation could be carried out.

It was pointed out previously (section IV) that the inflection point of the thermogram of a glass transition is not the actual transition temperature, but usually the surface temperature of the sample when the center undergoes the transition (assuming that the X axis records the block temperature). A few theories have been put forth in the literature to try to explain the heat transfer in a sample cylinder undergoing a glass transition, and thus develop means of predicting the actual glass transition temperature from a DTA thermogram.

Strella (90) tried to develop a theory for the correct interpretation of the glass transition temperature from DTA thermograms by application of Carslaw and

Jaeger's equation (9) for heat transfer in an infinite cylinder of radius "a" with the surface exposed to a heat flux increasing at a constant rate (T equal to zero when time t is equal to zero). Their equation for the temperature at radius r and time t is:

$$Tr = \beta (t - (a^2 - r^2)/4k) + (2\beta/ak) \left(\sum_{n=1}^{\infty} (J_0(r\alpha_n/\alpha_n^3 J_1(a\alpha_n)) \exp.(-k\alpha_n^2 t)) \dots \right)$$

By making the assumptions that values of α_n greater than α_1 are negligible and that $(J_0(0\alpha_1))/(\alpha_1^3 J_1(a\alpha_1))$ is approximately equal to $a^3/8$ (actually equal to $a^3/6.9$). The temperature difference between the surface and the center of the cylinder, at time t, is given approximately by:

$$\Delta T = (a^2\beta/4k)(1 - \exp.(-k\alpha_1^2 t)) \dots \dots \dots 31$$

At the transition temperature the thermal conductivity, changes from k_1 to k_2 causing the ΔT for the k_1 material to exponentially decay to zero while a new ΔT for the k_2 material develops. Therefore, if $t = 0$ when the surface temperature reaches the transition temperature:

$$\begin{aligned} \Delta T &= (a^2\beta/4k_2)(1 - \exp(-k_2\alpha_1^2 t)) + (a^2\beta/4k_1)(\exp.(-k_1\alpha_1^2 t)) \dots \dots \dots 32 \\ &= \text{developing } \Delta T \text{ for } k_2 \text{ material} + \text{decaying } \Delta T \text{ for } k_1 \text{ material} \end{aligned}$$

Thus it can be seen that by extrapolating a log Tg (indicated) vs. rate curve to zero rate the systems lags can be eliminated and the true Tg obtained (overlooking the assumptions made in the development of the theory). This curve, as seen from equation 32, is linear.

Haly and Dole (34) comment on a few errors in Strella's analysis. They point out that, by double differentiation of equation 32 with respect to time, the interval between the time the surface is at Tg and the time the center of the cylinder is at Tg, t_i , is obtained: $t_i = (\ln(k_1/k_2))/\alpha_1^2(k_1 - k_2) \dots \dots \dots 33.$

Thus, when the center of the cylinder is at temperature Tg, the surface temperature

is given by the equation :

$$T_{si} = T_g + \beta t_i \dots\dots\dots 34.$$

Since t_i is independent of β , equation 34 is a linear rather than a logarithmic relationship. The authors also take issue with Strella's assumption of a step change in k , believing the change to be of the S curve type. Using a curve of this type, obtained calorimetrically for polypropylene, they go through an iterative solution of the heat transfer, dividing the radius into four sections and assuming k is independent of r in each section. The value of t_i obtained from this analysis is much closer to a similar value obtained from the experimental data of Strella than to the value calculated using equation 33. This is attributed to the use of equilibrium values of k in a non-equilibrium situation.

Both papers overlook the poor assumption made in applying the equation of Carslaw and Jaegar, which is the basis of Strella's analysis and of equation 34 from the second paper. The former equation is for a situation where k is constant and the temperature across the cylinder is uniform at time $t = 0$. In a glass transition, k , of course, is not constant, but more important, at the start of a transition there is almost always a temperature profile across the cylinder.

In an attempt to explain the heat transfer in a DTA cell during a glass transition a little more fully, the following analogue computer program was undertaken.

1. Model

The following assumptions were made to enable the problem to be solved. These will be examined at the end of the description of the program for their applicability and effect on the results obtained.

- a. The temperature of the DTA block is the same throughout at any

given time. This allows the surface temperatures of the cylinders to be assumed constant around their circumferences.

b. The sample and reference materials are in the form of infinite cylinders.

c. The surfaces of each cylinder are exposed to a heating flux which increases at a steady rate.

d. The thermal conductivity, k , of the sample undergoes a step change at the glass transition.

Making these assumptions, the cylinder was divided into five radial sections so that Δr is 0.05 cm. in each case, and it was assumed that the temperature did not vary with r in these sections. Following the technique of Rogers and Connolly (78), the heat transfer equation: $\partial T / \partial t = k(1/r(\partial T / \partial r + \partial^2 T / \partial r^2))$ was modified to the set of finite difference equations:

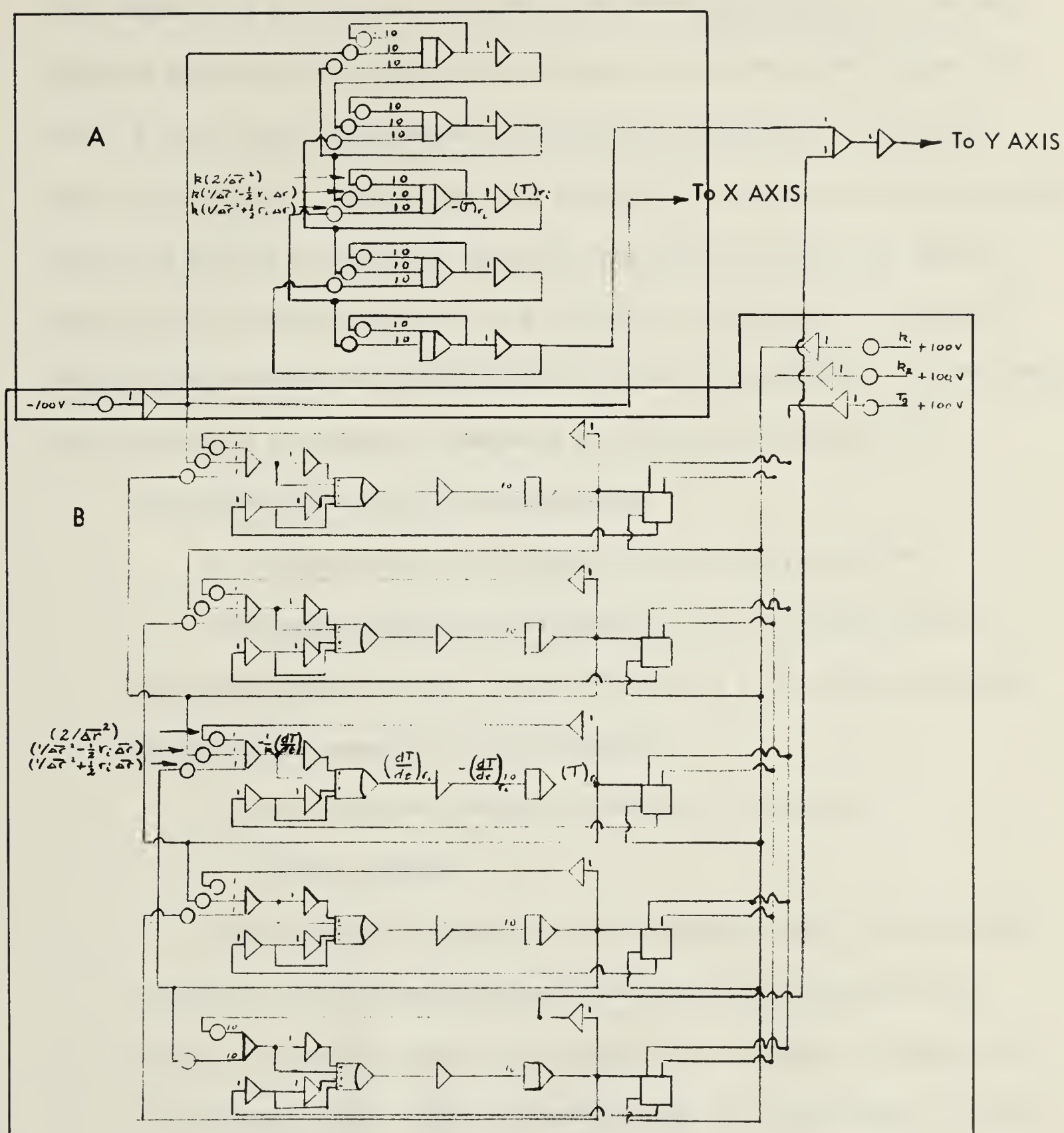
$$\begin{aligned} (dT/dt)_{r=r_i} = & k((1/\Delta r^2 + 1/2r_i \Delta r)T_{i+1} \\ & + (1/\Delta r^2 - 1/2r_i \Delta r)T_{i-1} \\ & - (2/\Delta r^2)T_i) \dots\dots\dots \end{aligned} \quad 35$$

where $i = 1$ to 4, $\Delta r \equiv (\Delta r)$ and for $i = 4$, $T_{i+1} = T_a$; and the equation:

$$(dT/dt)_{r_0} = k((4/\Delta r^2)T_1 - (4/\Delta r^2)T_0) \dots\dots\dots \quad 36$$

where r_0 is the center and r_a or a is the surface of the cylinder.

These equations were programmed for an analogue computer as shown in figure 16, section A being for the reference material and section B for the polymer sample. The portion occurring in both sections A and B represents the heat flux which heats the surface of both cylinders. The rate of heating can be varied by changing the value of the variac in the common section. Each row represents one



ANALOG SIMULATION OF HEAT TRANSFER IN DTA APPARATUS

SAMPLE UNDERGOING GLASS TRANSITION

FIGURE 16

radial segment and these segments are linked both forward and backward. The only difference between sections A and B is the means of multiplying by the k value. In section A, the k value is incorporated in the constants represented by the variacs before the integrators. In section B, the k values and the temperatures for each polymer segment are fed into a comparator. When the temperature of a particular segment reaches T_g , the comparator switches the k value from k_1 to k_2 , and this k signal is relayed to the multiplier for multiplication by the rest of the equation. Thus each segment goes through the transition in sequence as is the case in the actual DTA.

The original model should now be examined:

- a. The temperature of the block is uniform at any given time.

The thermal conductivity of the steel in the cell is several orders of magnitude greater than those of either the polymer or the reference material (Al_2O_3) so this assumption is quite reasonable.

- b. The sample and reference materials are in the form of infinite cylinders.

This is probably the most inaccurate assumption made. The cylindrical sample and reference materials, used in the experimental analysis on the Aminco Thermoanalyser, were of the order of one centimeter in diameter and one centimeter long. However, the base rested on a ceramic base, a thermocouple 0.2 cm. in diameter extended through the center of the cylinders for approximately one half of their length, and the tops were exposed to a diffusing atmosphere. To take all of these factors into consideration in a three dimensional heat transfer problem changing with time would be extremely difficult, and beyond the scope of this work. Therefore the

assumption of infinite cylinders had to be made in order to solve the problem at all.

- c. The surfaces of the cylinders are exposed to an even heat flux increasing at a constant rate.

This assumption depends upon the acceptance of assumption a, and the instrumentation on the power input to the furnace. It is quite valid in most DTA apparatuses.

- d. the k value of the polymer undergoes a step change at the glass transition

A step change in k seems to be a reasonable interpretation of the glass transition if it is assumed to be caused by the sudden initiation of molecular (chain) motion in the polymer. This view is opposed by Haly and Dole (34) who show the curve of k values for polypropylene going through the glass transition. The curve they show is like an inverted S with the transition in k values occurring over 40°K . However, an anomaly in these results must be pointed out. The data given is presumably for an equilibrium process, yet the transition occurs over forty degrees, while in a dynamic technique such as DTA the glass transition rarely covers more than ten degrees. In view of this discrepancy in data, and the fact that the analog program was made much simpler by assuming the step change, this assumption was used.

IX. RESULTS

A. Melting point determinations

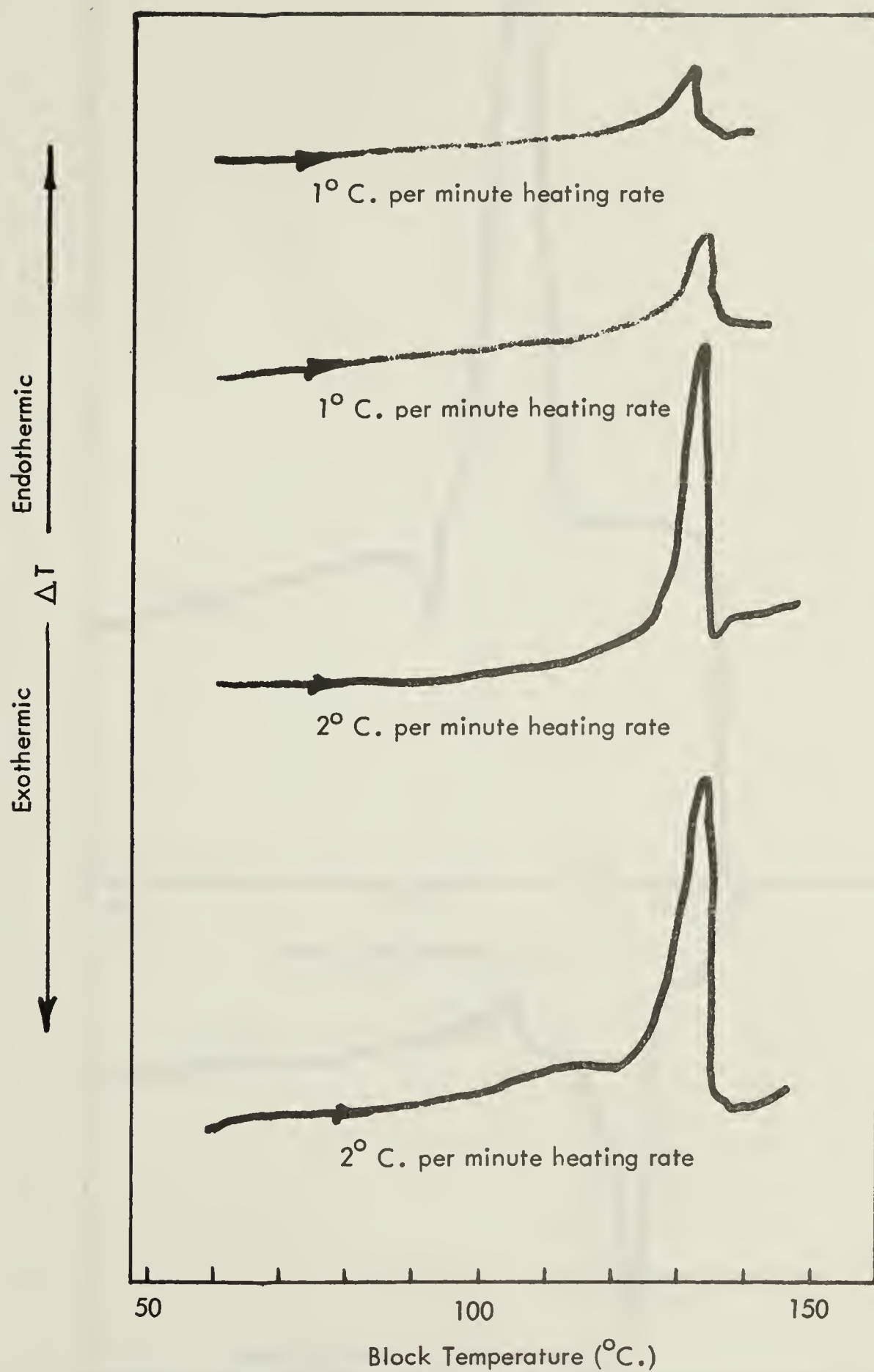
Figures 17, 18 and 19 show the thermograms produced, and table E gives the results obtained for the melting point determinations of polymers P and Q along with those obtained by Holden. Values of T_c , the crystallization temperature, have been included for reference, although they were not included in Holden's work (38). T_m is taken as the temperature at the top of the peak, just before the return to the baseline begins, and T_c is the temperature at the break in the baseline just before the peak starts (high temperature side of the peak),

TABLE E

RESULTS OF DTA MELTING POINT DETERMINATIONS

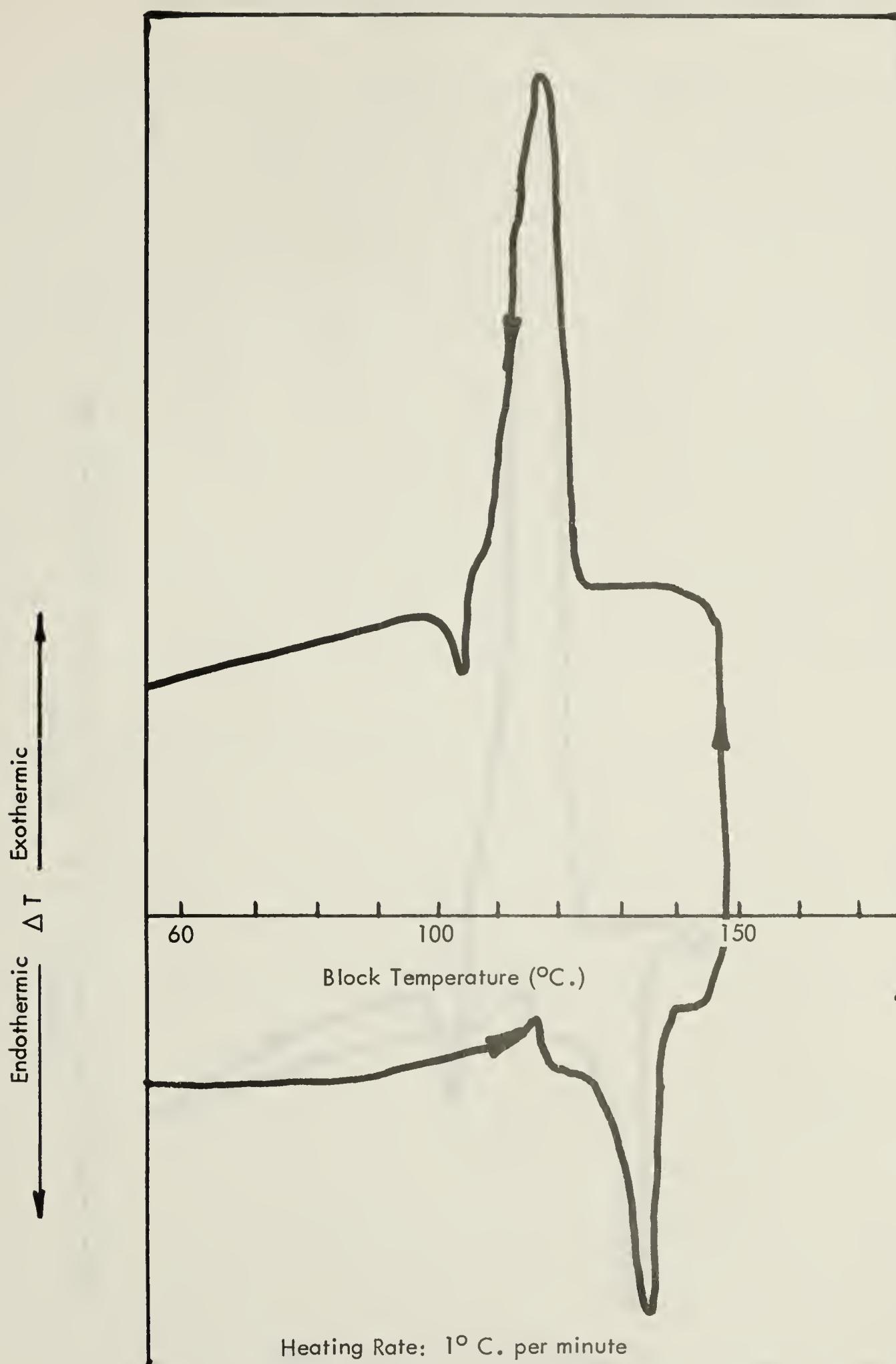
Polyethylene Sample	Test No.	Heating Rate °C./min.	T_m (°C.) This work/Ref.38	Cooling Rate °C./min.	T_c (°C.)
P	1	1	132.5 / 134	1/2	122
		1	134 / 134	1/2	122
	2	2	134 / 134	1.6	122
		2	134.5 / 132	8	123
		2	133 / 132	8	123
	3	1	134 / 134	1/2	123
		2	134.5 / 134	1/2	124
Q	3	1	116.5 / 114	1/2	107
		2	117 / 114	1/2	107

It is felt that the thermograms could be read to an accuracy of $\pm 1/2^\circ\text{C}$. in each case. Agreement for polymer P was quite good, with three of seven determinations checking exactly with those of Holden and the maximum deviation being 2.5°C . The use of polymer Q as the reference had no observable effect on the results.



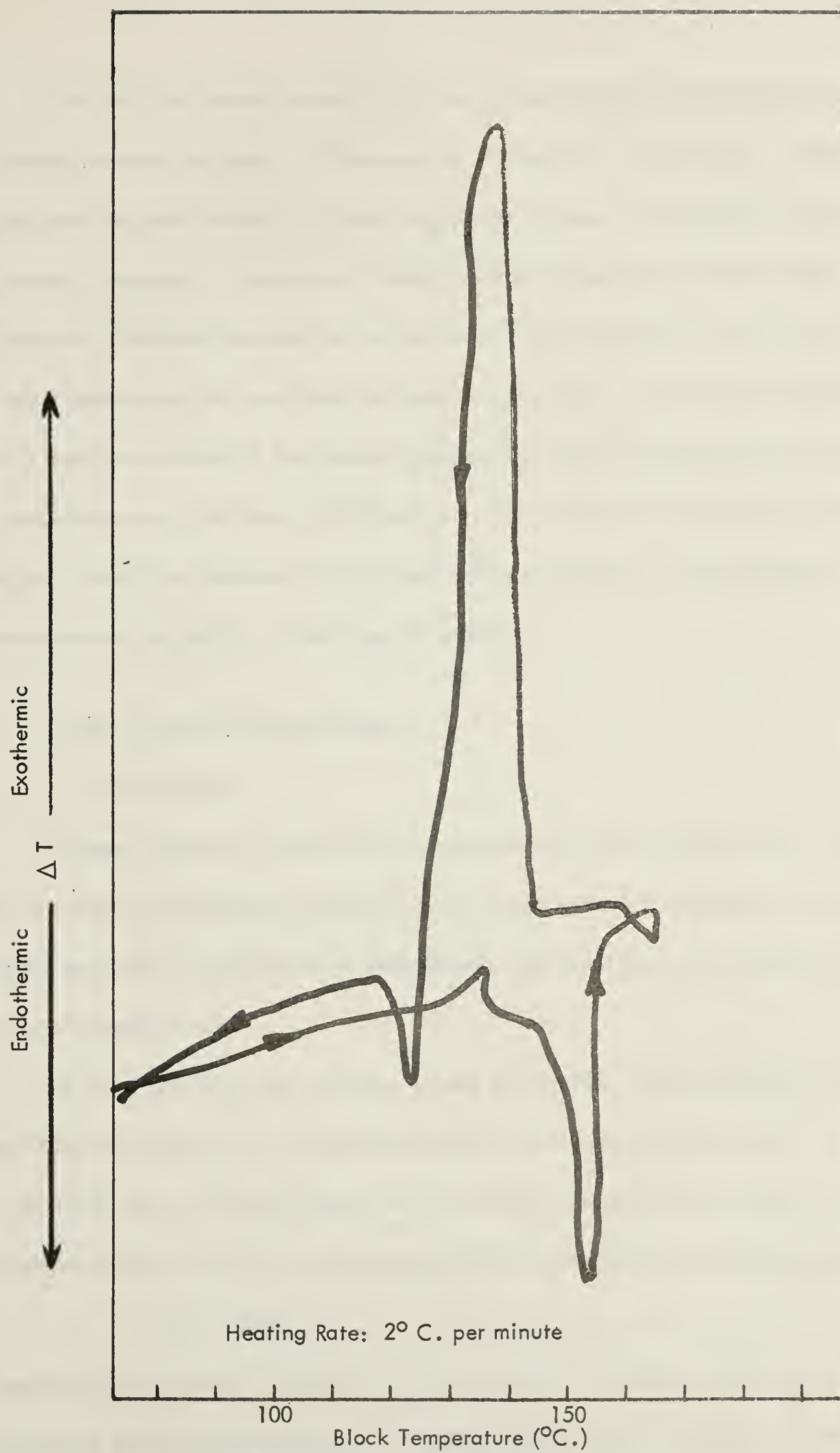
TYPICAL THERMOGRAMS OF THE MELTING TRANSITION
OF POLYMER P

FIGURE 17



TYPICAL 'COMPLETE' THERMOGRAM
OF POLYMERS P AND Q

FIGURE 18



TYPICAL 'COMPLETE' THERMOGRAM
OF POLYMERS P AND Q

FIGURE 19

The two runs made comparing polymer Q melting points with those obtained by Holden were not as good. Differences of 2.5 and 3°C. were noted. Also the double melting peak noted by Holden for polymer Q was not noticed in these determinations. However, in defence of these results, it should be pointed out that Holden only obtained one reading for polymer Q after cooling at 1/2°C. per minute, all other determinations coming after faster cooling rates. Also it can be seen in tests 1 and 2 on polymer P that determinations occurring under exactly the same circumstances can give results differing by 1.5°C. Over all, the Aminco Thermo-analyser, which was designed for soil and ceramic analyses, proved reasonably accurate when applied to the melting of polymers.

B. Glass Transition Determinations

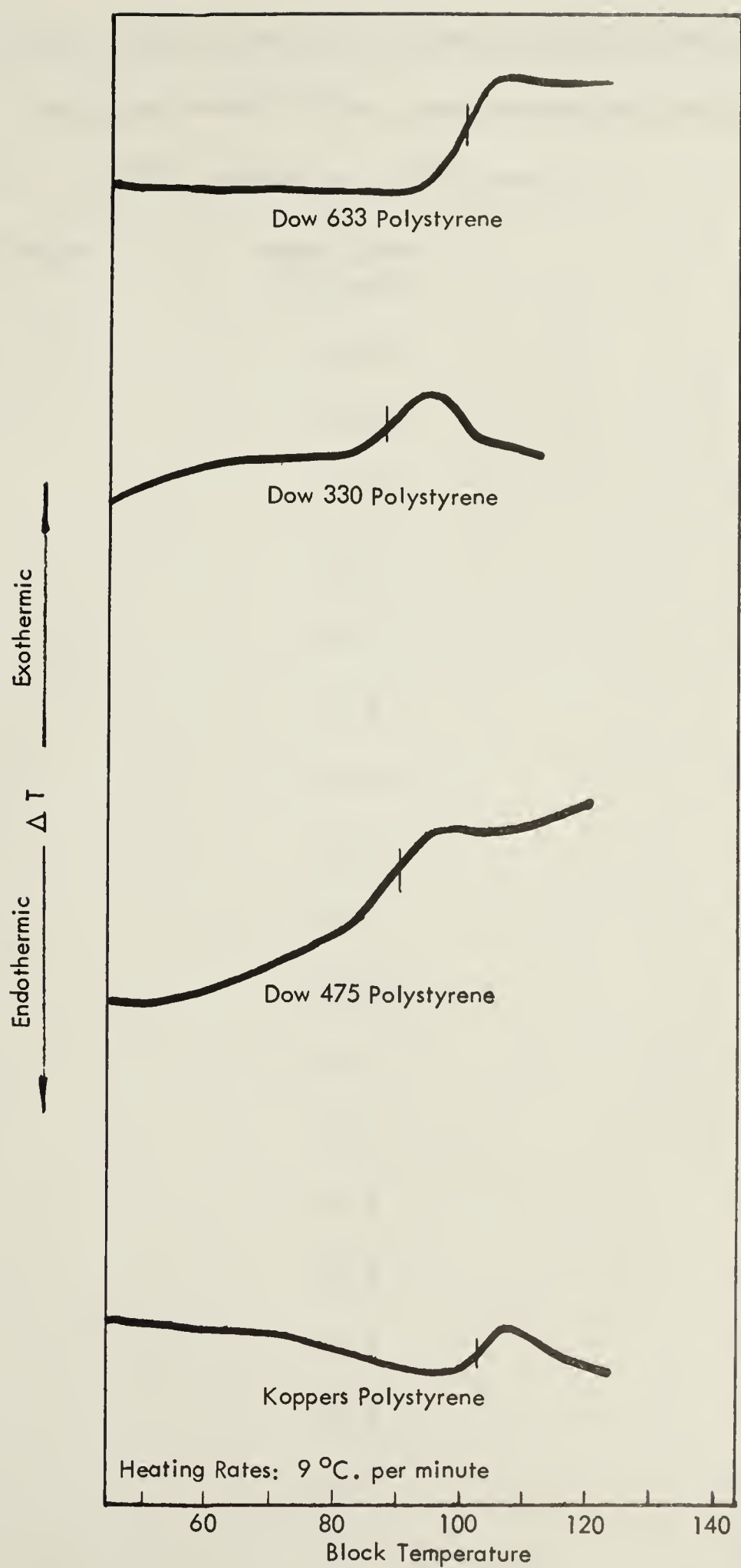
1. Polystyrene

Figure 20 shows characteristic thermograms produced, and tables F and G give the results obtained, for different heating rates and sample weights. A number of glass transition temperatures for polystyrene, obtained from the literature, are shown in Appendix one.

It was noted that the polymers formed two groups, Dow 330 and 475, and Dow 683 and Koppers, the former having lower T_g values than the latter. It was felt that this may have been due to their molecular weights so the viscosity average molecular weights of the four samples were calculated using the following equation:

$$[\eta] = KM^a \dots\dots\dots 30$$

where M is the molecular weight, $[\eta]$ is the intrinsic viscosity, and K and a are empirically determined constants. The values used were $K = 1.03 \times 10^{-4}$ and $a = 0.74$ (26). The results, shown on table H, indicate very close grouping of the



TYPICAL THERMOGRAMS OF THE GLASS TRANSITION
OF POLYSTYRENE
FIGURE 20

TABLE F

RESULTS OF DTA GLASS TRANSITION TEMPERATURE DETERMINATIONS

(All samples were approximately 100 mg., pretreatment was heating to 122°C. and cooling at 8°C./min.)

Polystyrene Sample	Heating Rate °C./min.	T _g °C.
Dow 330	12.3	91
	9.6	87
	6.3	89
	3.1	84
Dow 683	12.3	101
	9.6	103
	6.3	102
	3.1	102
Dow 475	12.3	90
	9.6	89
	6.3	89
	3.1	89
Koppers	12.3	105
	12.3	106
	9.6	104
	6.3	104
	6.3	103
	3.1	102
	3.1	101

TABLE G

EFFECT OF SAMPLE WEIGHT ON DTA GLASS TRANSITION POINT DETERMINATIONS

Polystyrene Sample	Weight milligrams	Heating Rate °C./min.	T _g °C.
Koppers	102	14.0	106
	150	14.0	107
	202	14.1	107

TABLE H

MOLECULAR WEIGHT DETERMINATIONS FOR POLYSTYRENE

Polystyrene Sample	Intrinsic Viscosity	Molecular Weight
Koppers	0.87	200,000
Dow 330	0.81	183,000
Dow 475	0.91	215,000
Dow 683	0.908	214,500

molecular weights. An inquiry to Dow indicated that samples 330 and 475 contained plasticizers, which accounted for the lower glass transition temperatures.

The T_g determinations show slight heating rate dependencies, but the scatter in the data is almost as great an effect. The reproducibility of the results appears to be $\pm 1^\circ\text{C}$ on the basis of the Koppers data, but the effect of the heating rate appears quite different with each set of data.

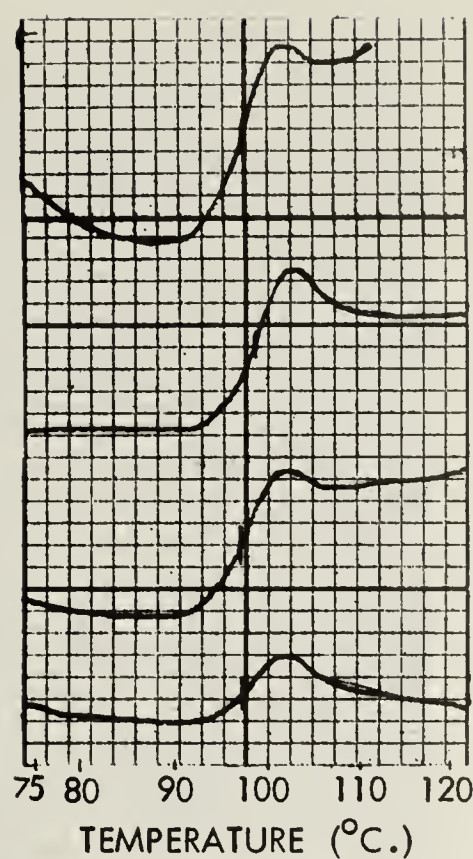
The effect of the sample weight is negligible, as shown on table 5.

The extreme range of literature values, shown in Appendix one, makes comparisons impossible so it can only be said that these results are in the correct "ball park" for the glass transition of polystyrenes.

A check of the data reproducibility was also made. The samples were heated and cooled for five cycles at each heating rate and the curves compared. The results are shown on figures 21 and 22. The agreement in any one set is extremely good, but no definite differences could be observed in the transition temperatures with changing rates.

2. Copolymers

A few typical thermograms are shown on figure 23 while tables I and J show the glass transition temperatures determined for the copolymers at varying heating rates. The reproducibility of the results varies from cases where the same temperature was obtained for tests under the same conditions, to cases where there is eight degrees difference between the two readings. This is attribute chiefly to the difficulties involved in determining which curve in the baseline was actually the glass transition. The thermogram of the glass transition has a characteristic shape, and is usually sharper than curves caused by uneven heating in the block. However,



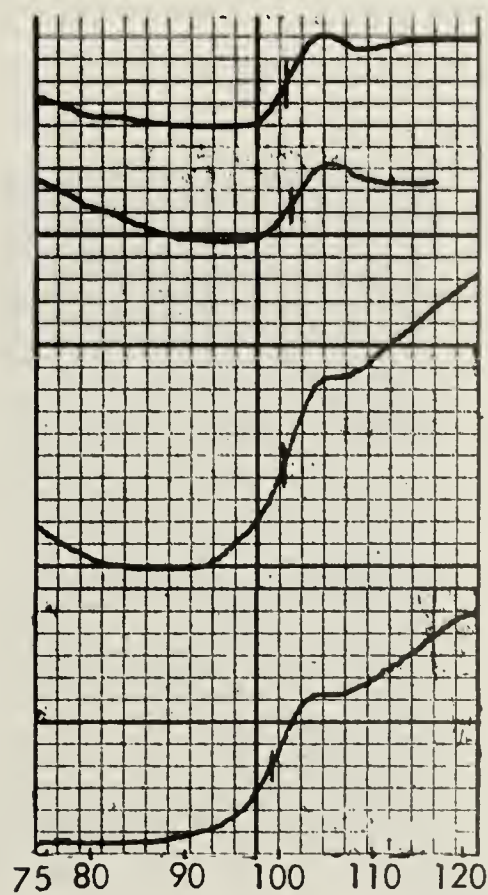
Heating Rate 0.097 °C./sec.

Cooling Rate

Between Runs 0.091 °C./sec.

Y Axis Amplification 0.05 °C./inch

Y Axis Amplification 0.10 °C./inch



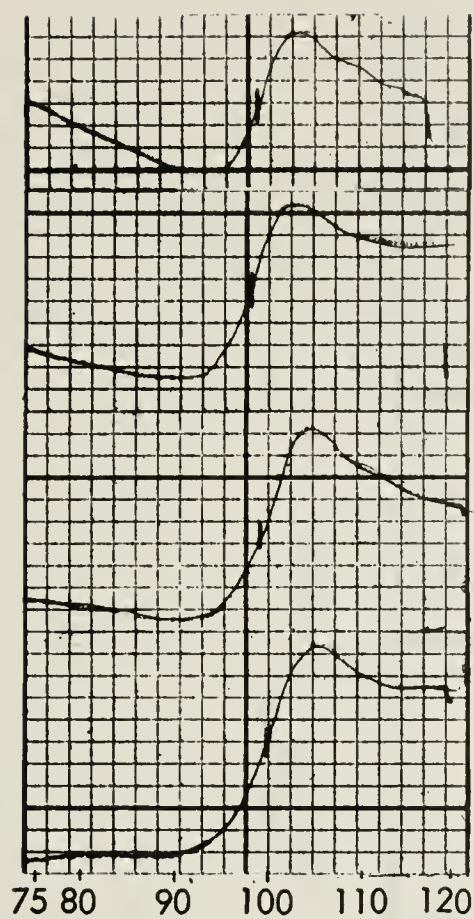
Heating Rate 0.052 °C./sec.

Cooling Rate

Between Runs 0.091 °C./sec.

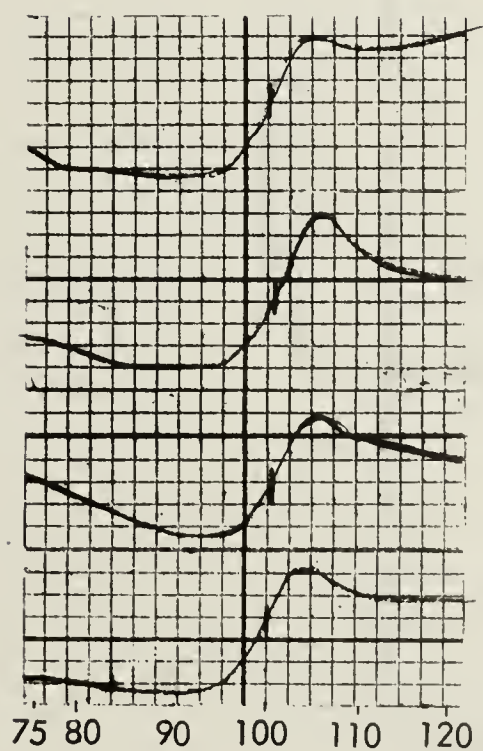
Y Axis Amplification 0.05 °C./inch

SAMPLE: DOW 683 POLYSTYRENE
FIGURE 21



Heating Rate 0.205 °C./sec.
Cooling Rate
Between Runs 0.091 °C./sec.

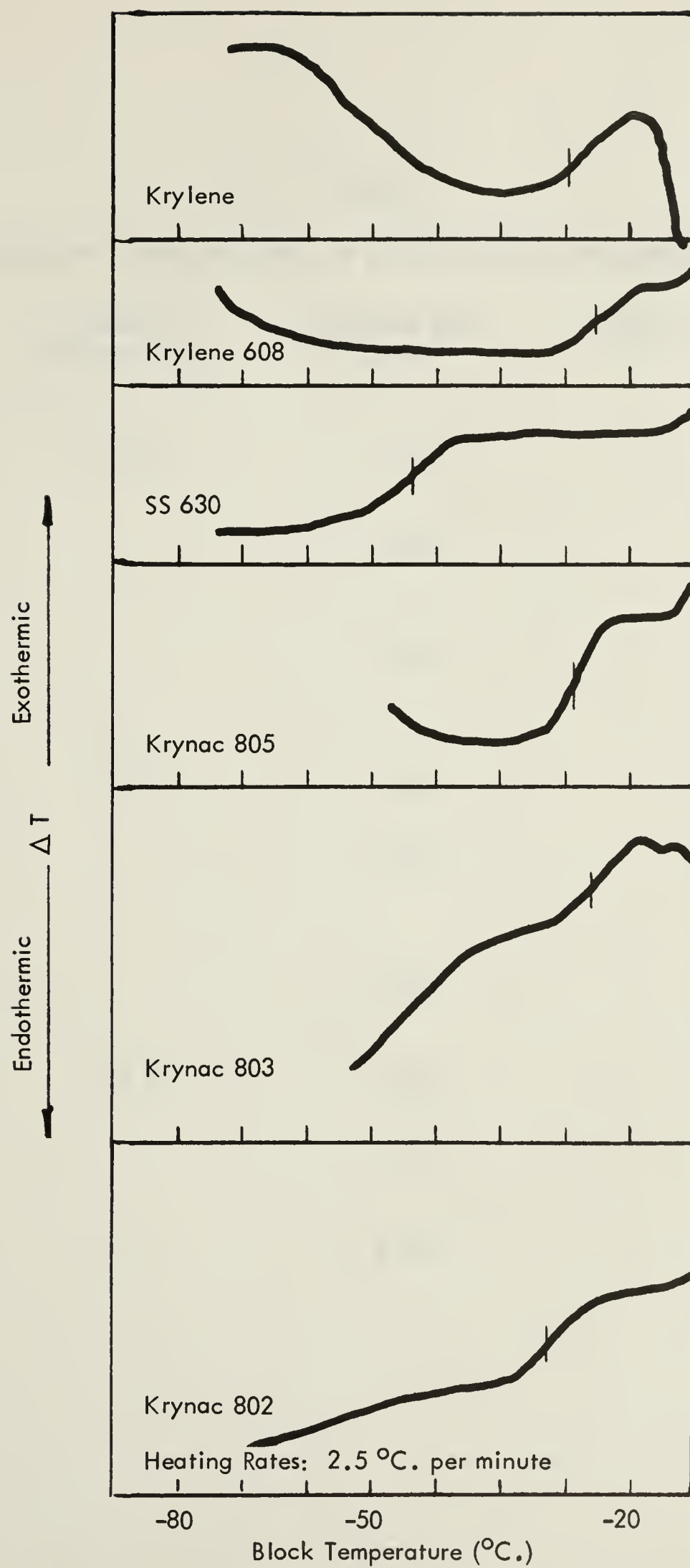
Y Axis Amplification 0.1 °C./inch



Heating Rate 0.150 °C./sec.
Cooling Rate
Between Runs 0.091 °C./sec.

Y Axis Amplification 0.1 °C./inch

SAMPLE: DOW 683 POLYSTYRENE
FIGURE 22



TYPICAL THERMOGRAMS OF THE GLASS TRANSITION
OF COPOLYMERS
FIGURE 23

TABLE I

GLASS TRANSITION TEMPERATURES OF BUTADIENE-ACRYLONITRILE COPOLYMERS

Copolymer	Weight % Acrylonitrile	Heating Rate °C./sec.	Glass Transition Temp. (°C.)
Krynac 805	39.9	1.55	-16.0
			-22.0
		2.15	-18.0
			-19.0
		3.15	-18.5
			-19.5
Krynac 803	35.3	1.55	-24.0
		2.15	-21.0
			-21.0
		3.15	-27.5
			-22.5
Krynac 802	27.6	1.55	-24.0
		2.15	-21.0
			-29.5
		3.15	-22.5
			-23.5

TABLE J

GLASS TRANSITION TEMPERATURES OF BUTADIENE-STYRENE COPOLYMERS

Copolymer	Weight % Polystyrene	Heating Rate °C./sec.	Glass Transition Temperature	
			(a) Unextracted	(b) Extracted
Krylene	23.8	1.55	-51.5	-50.5
		2.15	-43.0	-48.0
		3.15	-48.0 -46.5	-53.0
Krylene NS	27.8	1.55	-37.0	
		2.15	-41.0	-37.0
		3.15	-41.5 -44.5 -45.0 -45.5	-32.5
SS630	27.9	1.55	-50.0	-45.0
		2.15	-43.5	-42.5
		3.15	-46.0	-48.0
Krylene 608	46.8	1.55	-12.0	-24.0
		2.15	-18.0 -19.0	-21.0
		3.15	-10.0 -14.0	-15.5

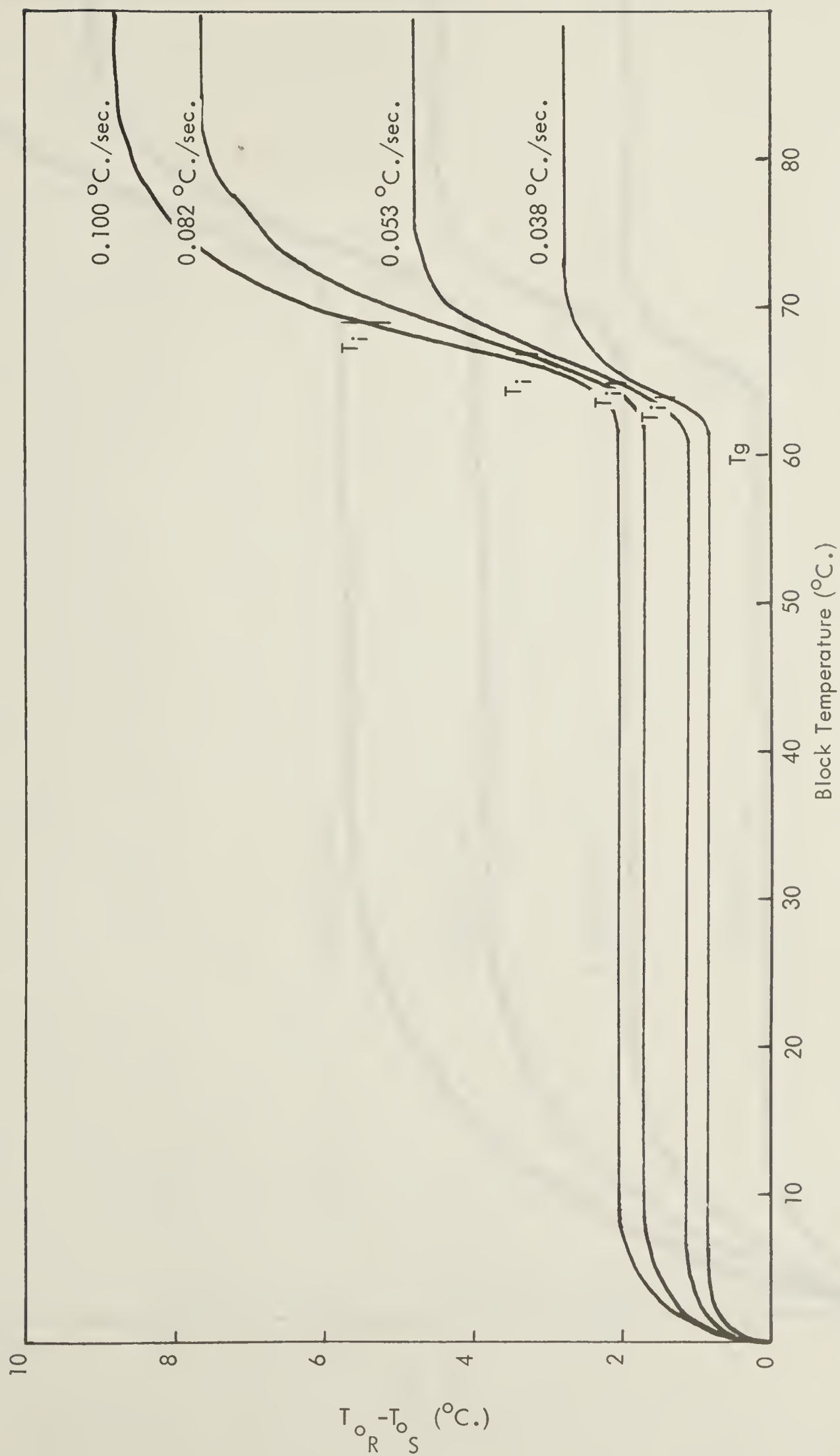
in some cases it was very difficult to pick out the glass transition and the estimated transition temperature in these cases would not be very accurate. An average scatter of $\pm 5.5^{\circ}\text{C}$. was found for the copolymer transition temperature readings.

The glass transition temperatures of the extracted butadiene-styrene copolymers were not consistently higher, as was expected, but all were within the scatter of the data so no conclusions can be drawn from this fact.

C. Interpretation of the Thermograms

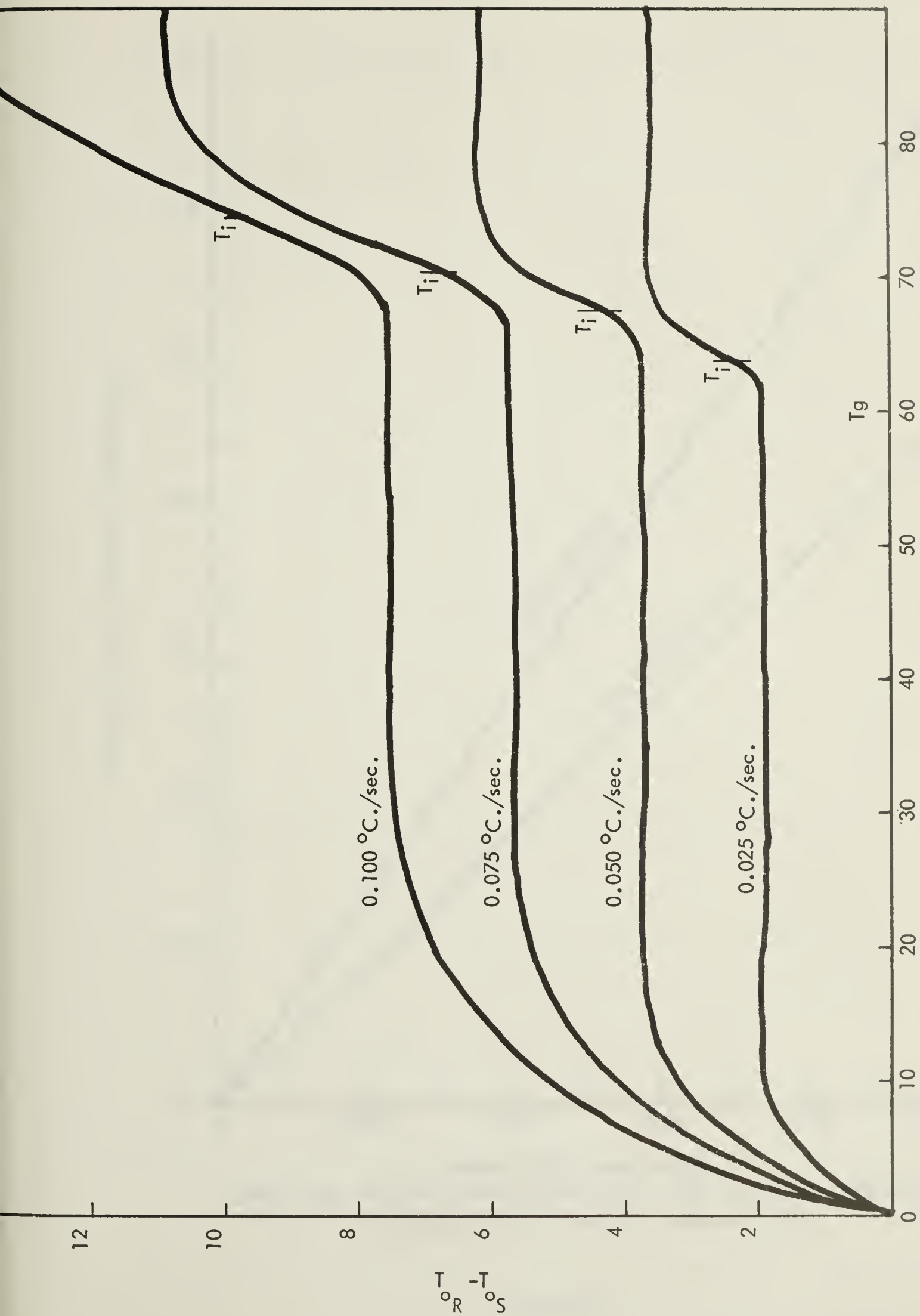
The analog program described previously, (section VIII), was run for the cases of polystyrene, with the k values changing from $1.15 \times 10^{-3} \text{ cm}^2/\text{sec}$. to $0.83 \times 10^{-3} \text{ cm}^2/\text{sec}$. (95), and polypropylene, with the k values changing from 1.6×10^{-3} to $1.0 \times 10^{-3} \text{ cm}^2/\text{sec}$. (34), on the Pace 231R computer belonging to the Electrical Engineering Department of the University of Alberta. The results, plotted by an X-Y plotter, are shown in figures 24 and 25. As can be seen, they are very much like the curves obtained from an actual DTA. Plotting the surface temperature at the time when the transition reached the center section (as marked on the curves) vs the heating rate, gave a straight line passing through the transition temperature at zero rate, as shown in figure 26. Thus it is shown that the indicated transition temperatures are linearly dependent upon the heating rate.

It was felt that some relationship should exist allowing the true transition temperature to be determined from a single thermogram. The equation from Strella's work (90) for the steady state temperature difference ($\Delta T = a^2 \beta / 4k$) could be used if the value of k at the transition point were known, as the surface temperature is obtained from the thermogram the heating rate is known and the radius is a constant.



ANALOG SIMULATION OF THERMOGRAMS OF THE GLASS TRANSITION OF POLYPROPYLENE

FIGURE 24



ANALOG SIMULATION OF THERMOGRAMS OF THE GLASS TRANSITION OF POLYSTYRENE

FIGURE 25

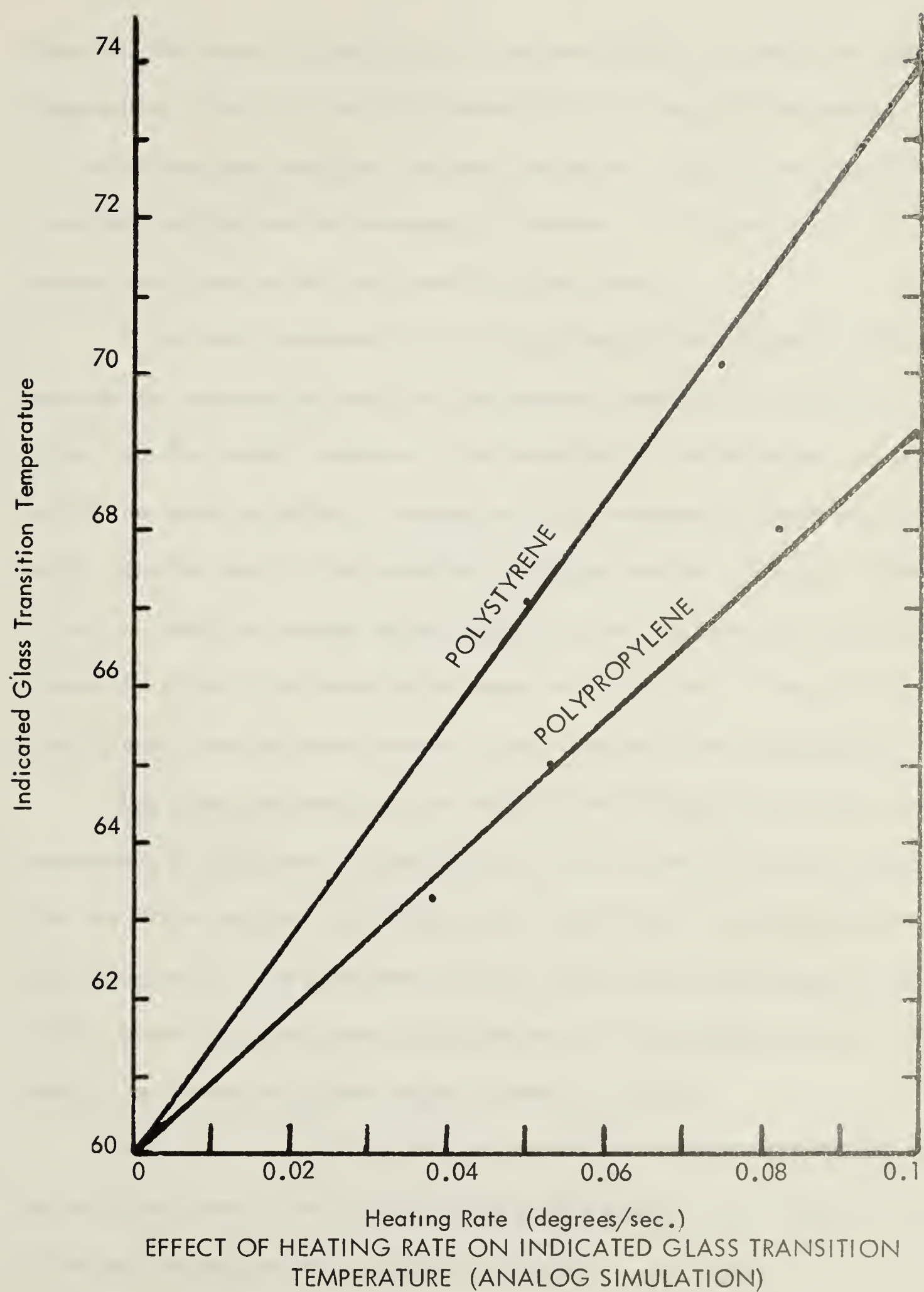


FIGURE 26

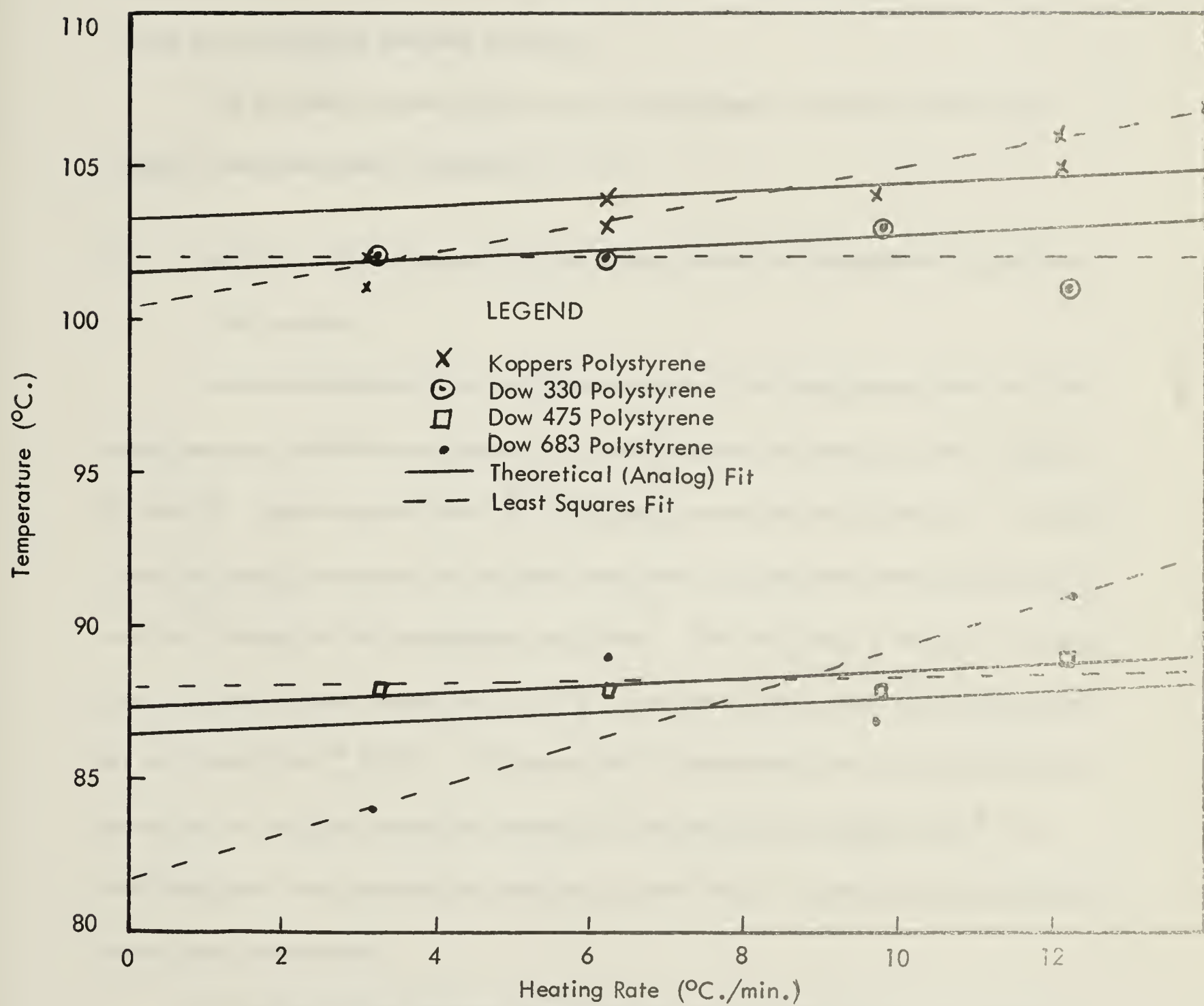
However, the thermal conductivity of the polymer may not be known at the transition temperature. Even if a curve of the thermal diffusivity versus the temperature for the polymer were available, the value changes very rapidly in the area of the transition, and the transition temperature is unknown. (This is assuming the S shaped curve shown by Haly and Dole (34) in their work.)

A relationship between $T_a - T_o$ for the polymer and the temperature difference between the centers of the sample and the reference materials, the ΔT of the thermogram, was then sought. However, it was found that the ΔT values are very small, so that the normal variations in choosing the X axis temperature, due to the choice of the inflection point on the thermogram, are larger than the ΔT values. Therefore it was concluded that the best method of obtaining the true T_g from DTA results is from a plot of the T_g (indicated) values versus the heating rate, at the point of zero heating rate. Thus the errors involved in any one value can be compensated for.

This theory was tested using the results of the DTA tests for the glass transition temperature of polystyrene. Figure 27 shows that the scatter in the data is greater than the differences due to the heating rate, as determined in the analog analysis. The extrapolation of the experimental data by a least squares technique is within $\pm 1^\circ\text{C}$. of the theoretical curve in all cases except for Dow 683 polystyrene. This sample also showed the greatest degree of scatter in the data.

If the DTA apparatus is so arranged that the X axis reference temperature can be that of the center of the reference material, the 'true T_g value is simply the T_g (indicated) value minus the ΔT value at that point.

In order to find the theoretical effect of placing the X axis reference thermocouple in the polymer sample, the results of the analog program were modified. It



EFFECT OF HEATING RATE ON INDICATED GLASS TRANSITION
TEMPERATURE OF POLYSTYRENE SAMPLES

FIGURE 27

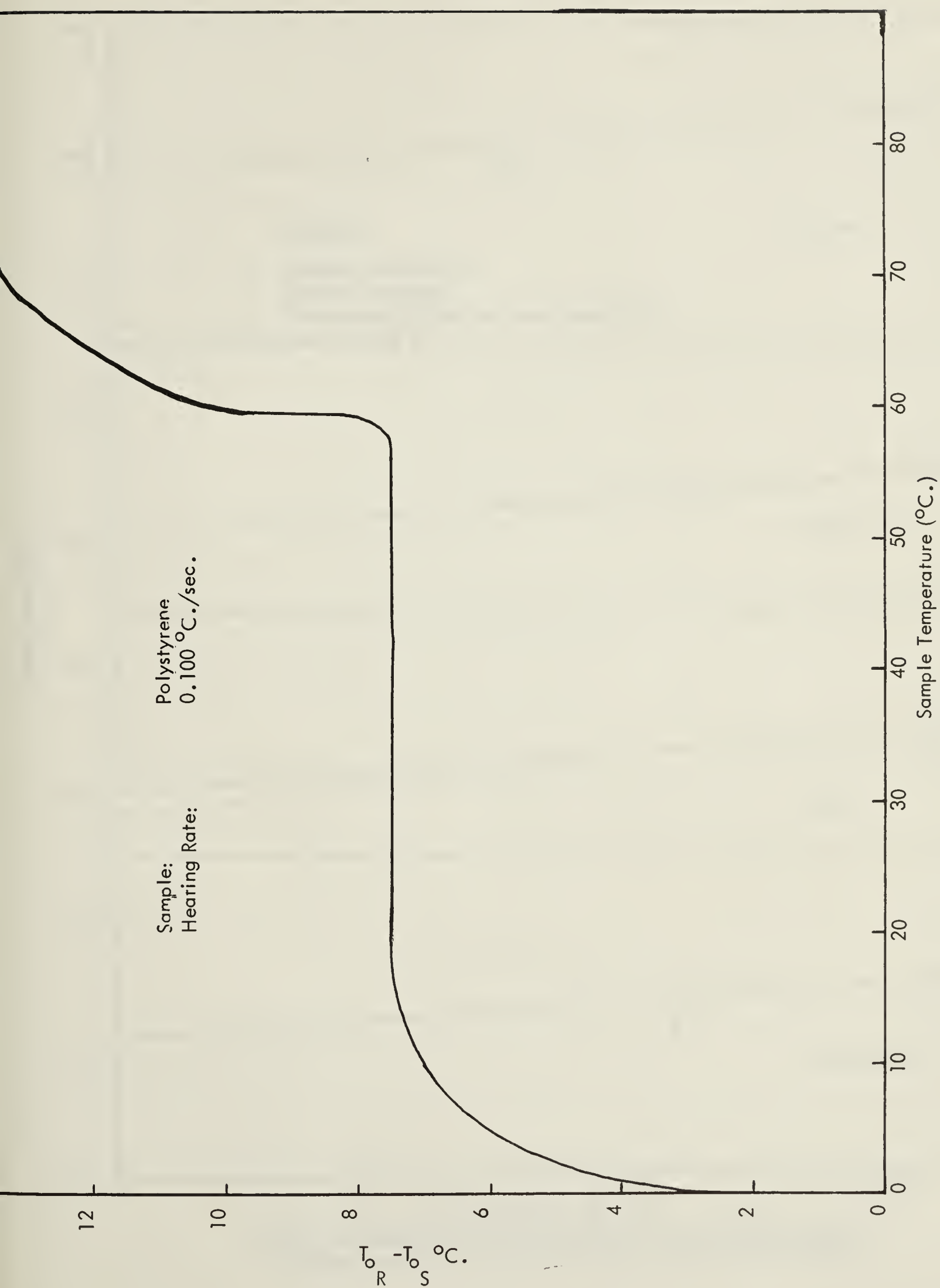
was assumed that for equal surface temperature changes between the start of the transition curve and the transition point, the effective thermal diffusivity changes in equal increments. The extrapolated curve is shown in figure 28. Thus, theoretically, the true T_g value can be read off of the thermogram directly as the point where the thermogram becomes vertical.

The problems caused by this type of arrangement in actual practice have already been described in section IV, C, 2.

D. Analysis of Copolymers Using the Glass Transition Temperature Found from DTA Analysis

The data obtained from the DTA analyses of the butadiene-styrene and the butadiene-acrylonitrile copolymers are plotted against the heating rate in figures 29 and 30. Least squares fits of the points, and theoretical relationships - estimated from the analog simulation of the glass transition of polystyrene and polypropylene, and the k values of the copolymers - are shown. The data show a maximum deviation from the least squares curves of $\pm 2.1^\circ\text{C}$. but the values cannot be considered to be any better than $\pm 5.5^\circ\text{C}$. This deviation is reasonable when it is noted that the deviation in the glass transition readings of the polystyrene samples was $\pm 1^\circ\text{C}$., and these tests were carried out under much more ideal circumstances and producing quite good thermograms.

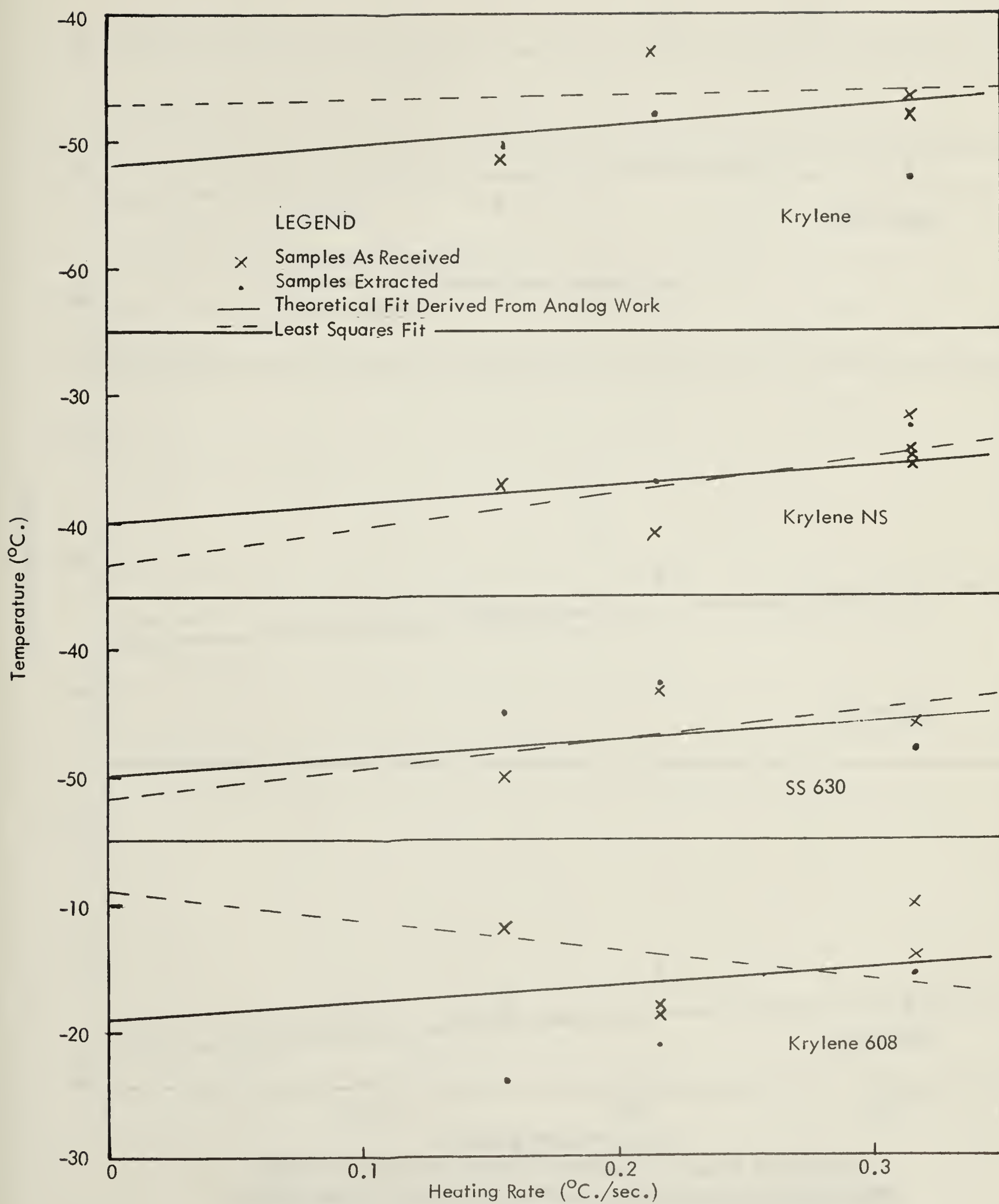
The values of the intersection of the theoretical (analog) curves with the zero rate axis were used for comparison with the various theoretical curves relating the copolymer composition with the transition temperature. These values were chosen because in most cases the fit of the analog curve was almost as good as the least squares fit, and the former curve had theoretical justification.



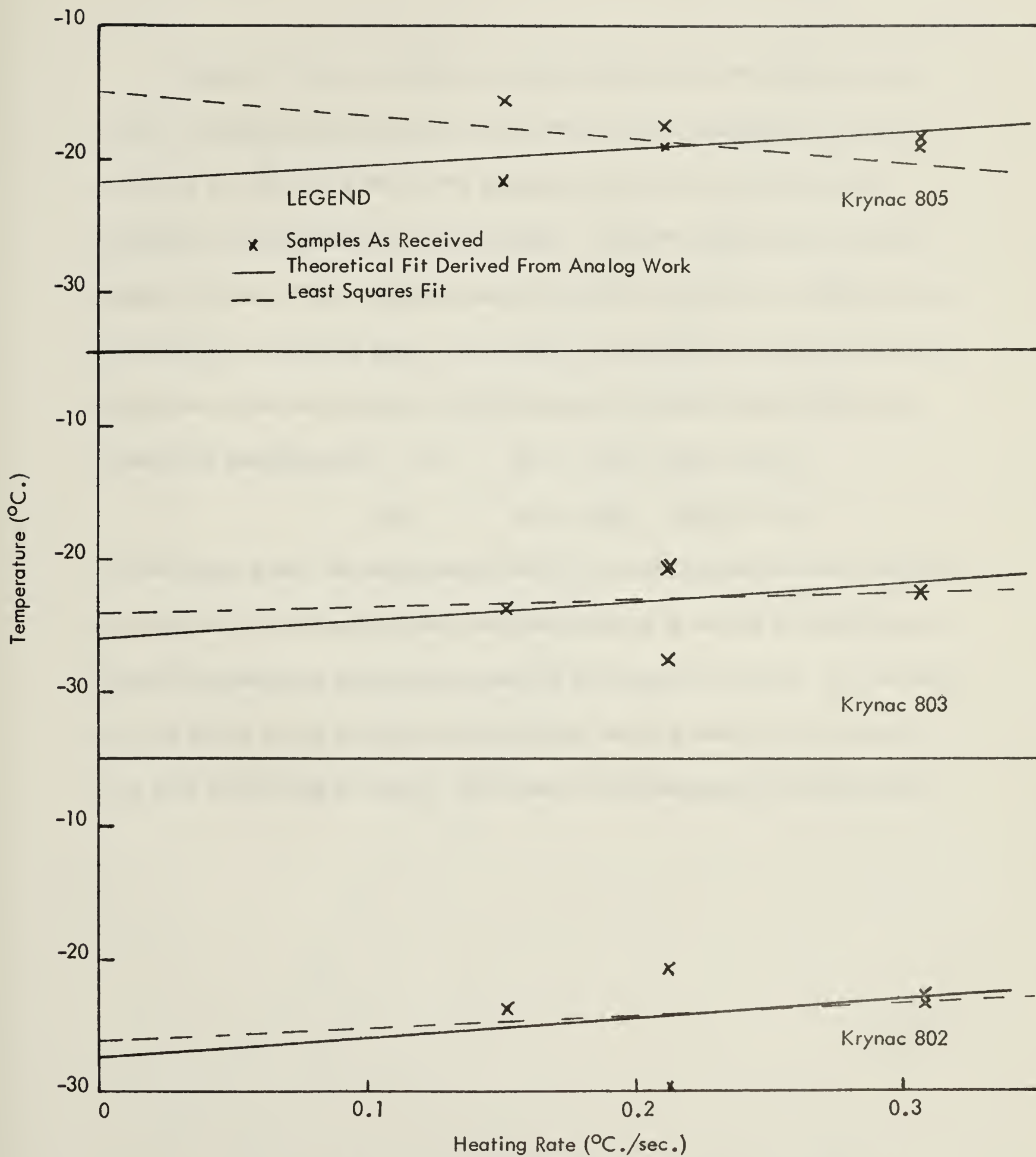
ANALOG SIMULATION OF THE EFFECT OF USING THE SAMPLE TEMPERATURE TO DRIVE THE X AXIS

FIGURE 28

FIGURE 29



EFFECT OF HEATING RATE ON INDICATED GLASS TRANSITION TEMPERATURE OF POLYSTYRENE-BUTADIENE COPOLYMERS



EFFECT OF HEATING RATE ON INDICATED GLASS TRANSITION
TEMPERATURE OF POLYACRYLONITRILE-BUTADIENE COPOLYMERS
FIGURE 30

Figures 31, 32, and 33 show the data obtained from the tests using the Aminco Thermoanalyser, along with other literature data compared to curves of equations 21, 25, 27 and 28; for the systems styrene-butadiene, acrylonitrile-butadiene, and polyethylene-polypropylene. The latter system was included to compare the only other copolymer analysis by DTA in the literature (108) with the experimental work of this paper. As an added comparison, the values of the styrene butadiene system were compared with the equations used by Wood (102) for his linear plots (see figure 34), i.e.

$$\begin{aligned} &T_g \text{ v.s. } (T_g - T_{g1})(1-C_1)/C_1 \\ &\text{and} \quad T_g \text{ v.s. } (T_{g2} - T_g)(C_2/(1-C_2)) \end{aligned}$$

On the former plots, the experimental data is as consistent and as close to any of the theories as the literature data, and also compares as well as Wunderlich and Poland's polyethylene polypropylene data to the theoretical curves. On the latter plot the results do not correlate at all although the data used by Wood shows up very well on this type of a plot. No reason for this discrepancy could be found.

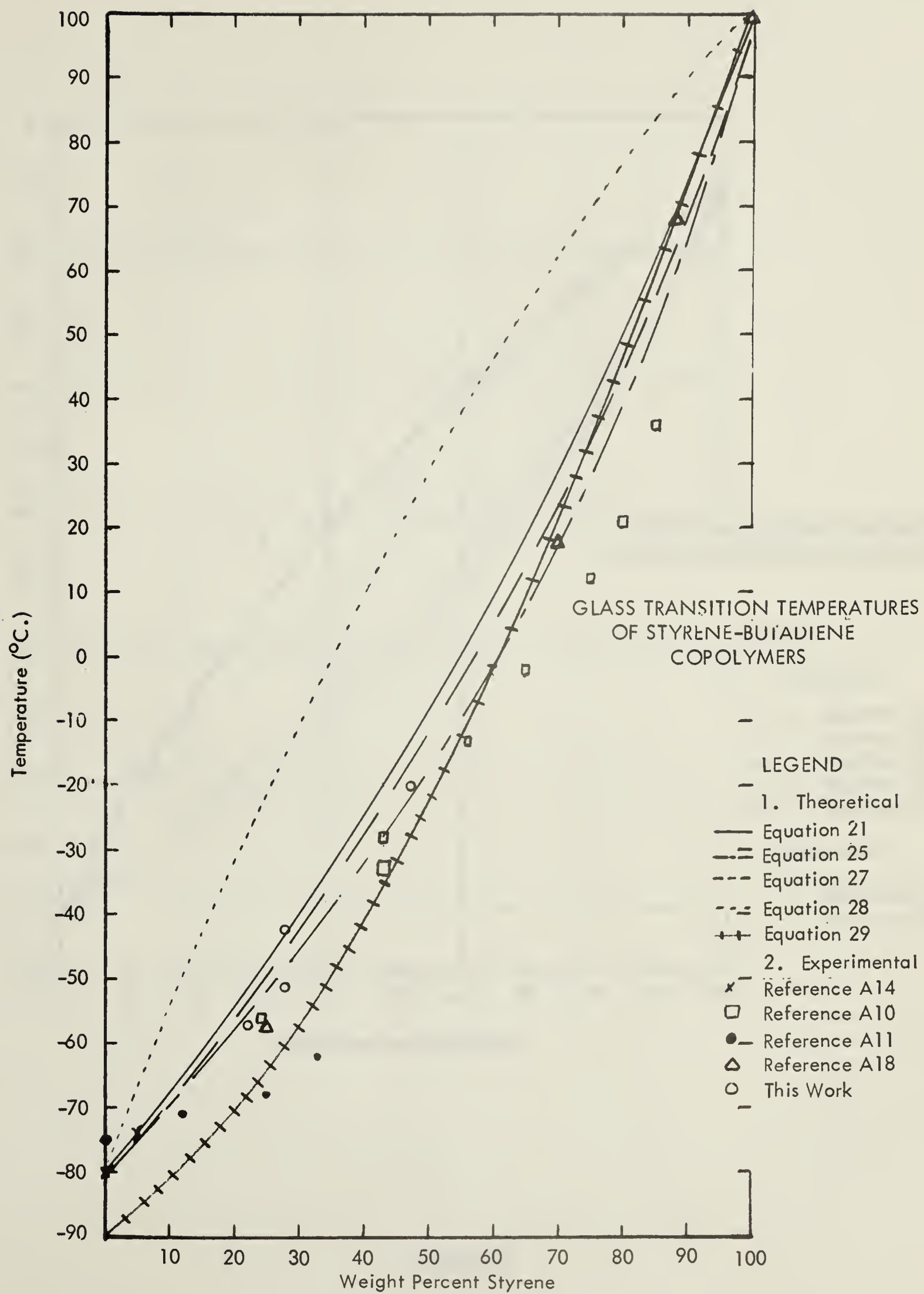


FIGURE 31

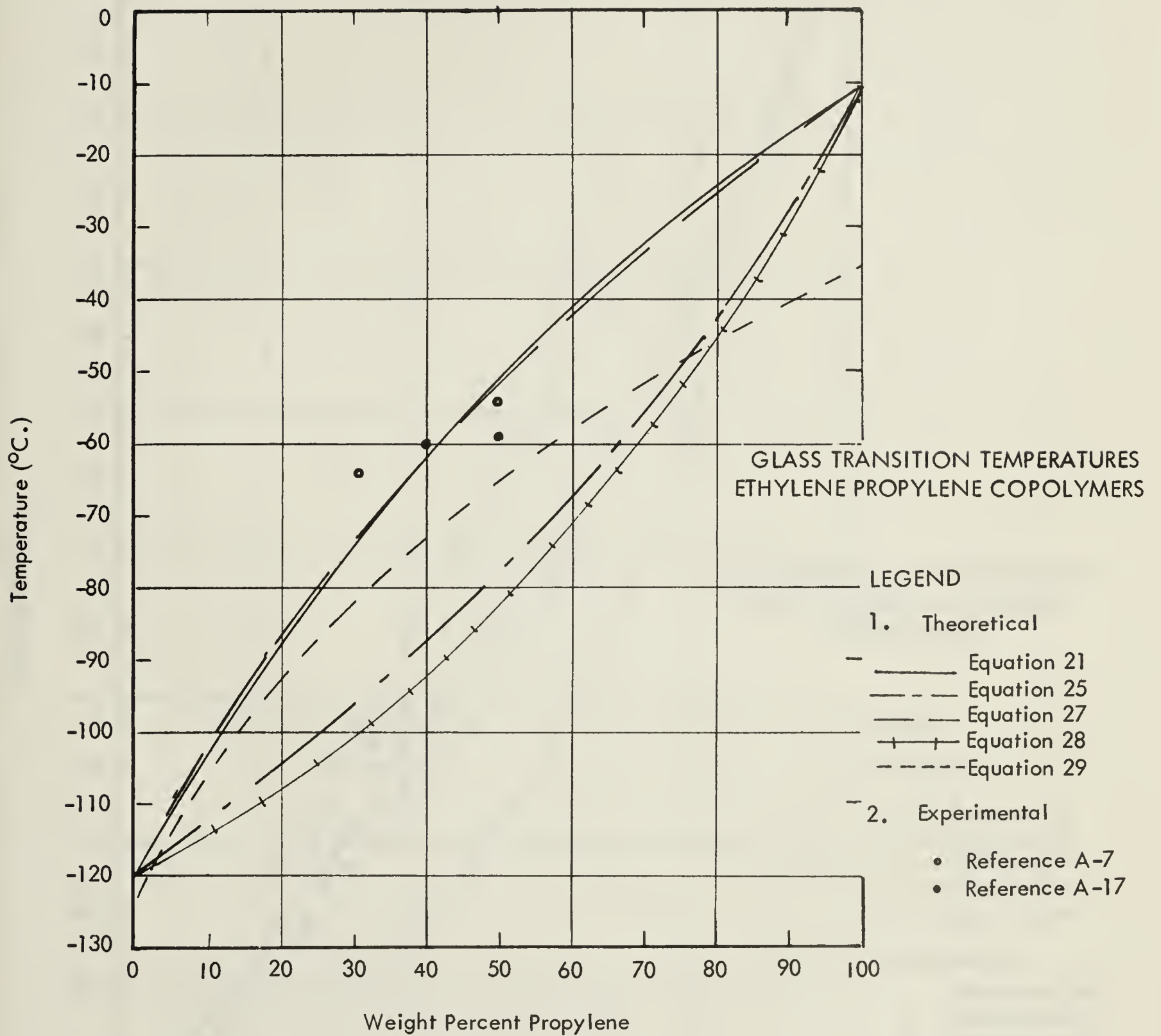


FIGURE 32

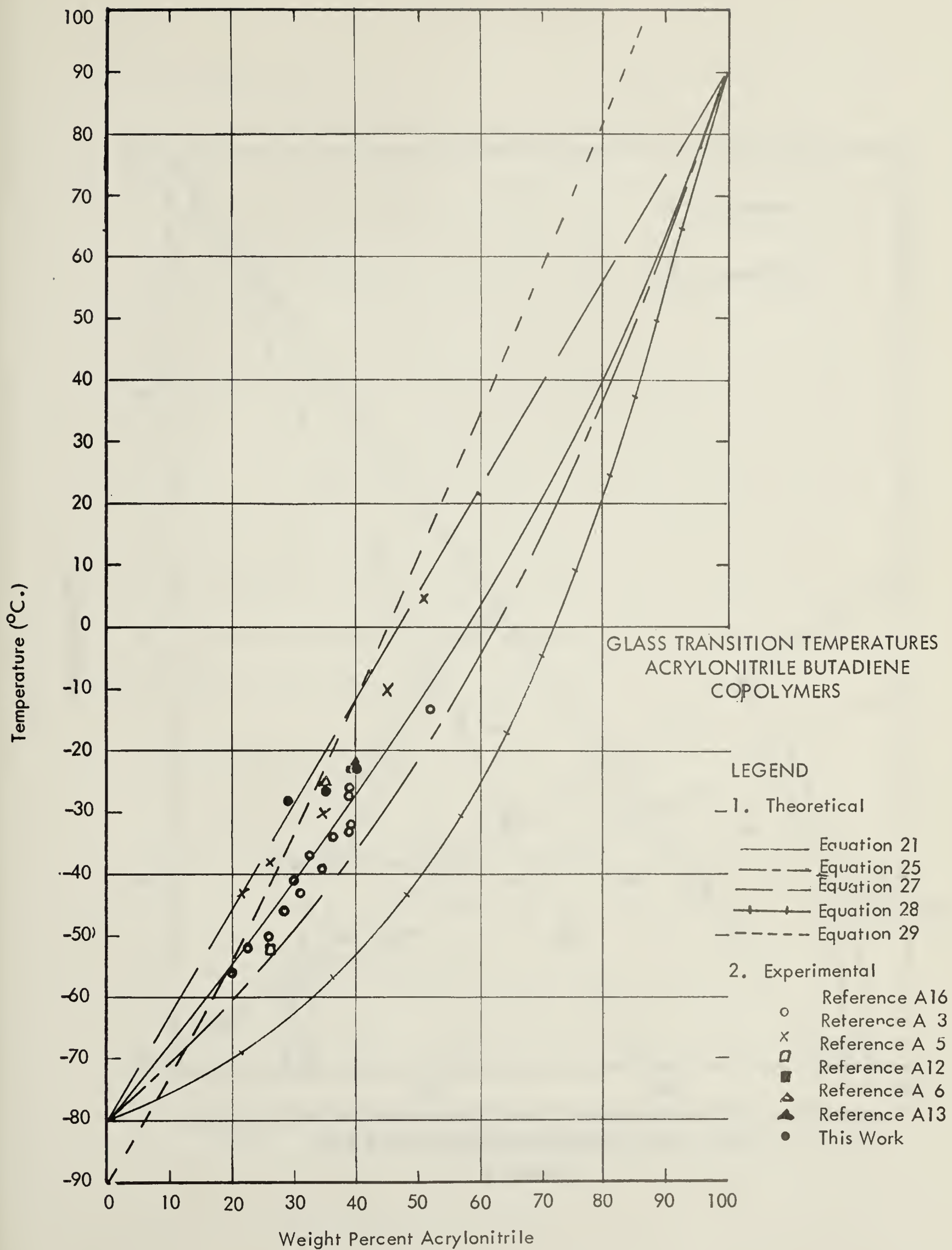


FIGURE 33

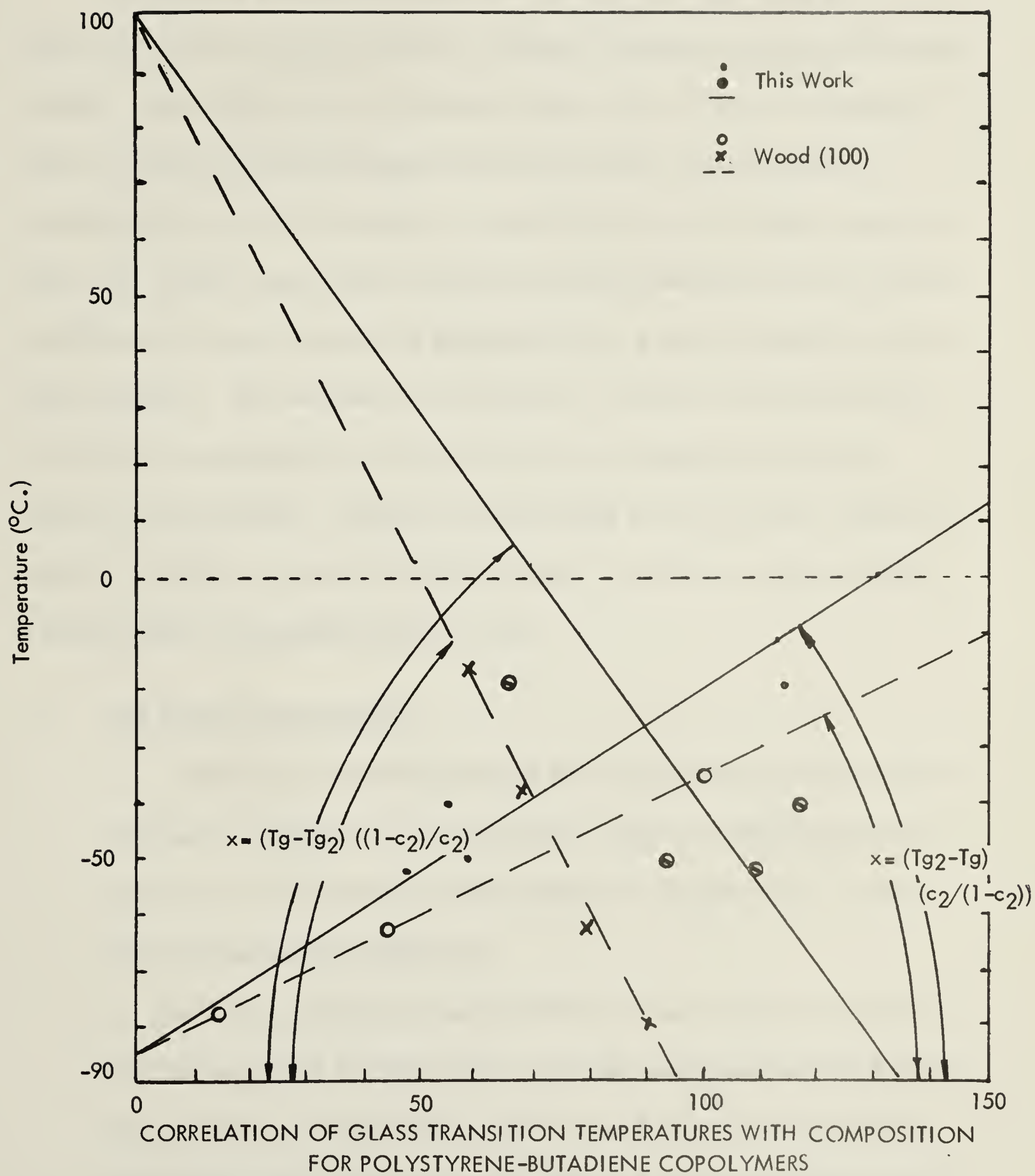


FIGURE 34

X. CONCLUSIONS

The complex structure of polymers has been examined, showing that even within a given molecule there are a number of configurations and conformations possible. These differences, on the broader level, lead to different morphological forms: crystallites of varying degree of packing and size, glassy and rubbery amorphous states and the liquid state - a less viscous form of the rubbery amorphous state. All of these forms exhibit a number of transitions between and with-in states, and differential thermal analysis has been examined as a means of obtaining data on these transitions. DTA has been seen to have many drawbacks, mostly concerning the degree and reproducibility of the heat transfer and temperature measuring abilities of the equipment. However, the advantages of the technique, chiefly the rapidity of the tests, overcome the disadvantages in a number of cases to give DTA a definite place in the polymer analysis field.

A. The Aminco Thermoanalyser

The Aminco Thermoanalyser used for the experimental work involved in this topic was designed for soil and ceramic analyses and does not have the accuracy and resolution to be really effective for polymer work. Its major faults and suggested remedies are:

a. The furnace and block sit too high above the panel they are attached to which allows either or both to lean to one side causing uneven heat distribution to the cells. The solution - build a new, shorter furnace and shorten the thermocouples entering the block. Ideally the block should be no more than four to six inches above the panel.

b. The thermocouples themselves are too large and must cause a considerable heat drain from the cells. The best improvement would be to have the thermocouples entering the top of the cells and use a jig for positioning the thermocouples in the polymer melt during the pretreatment. The thermocouples would have to be only stiff enough to be placed in liquid samples without moving. This change would also allow the use of cups for material containers to prevent the leaking of liquid samples into the cells, but it would do away with the heat transfer lag between the cup and the thermocouple.

c. A circulation system should be set up through either the block or the furnace, or both, for the circulation of a coolant through the system to give equilibrium cooling in the range of -50 to -75°C . This would be a difficult job and would only be needed if work was continued on the analyses by using the glass transitions or other work below ambient temperatures.

d. In cooling below ambient temperatures liquid nitrogen should be used in place of liquid air, as it was found that the oxygen in the liquid air oxidized the element in the furnace of the Aminco Thermoanalyser.

B. Uses of DTA for Examining First Order Transitions

1. Difficulties Encountered

The main disadvantages to the use of DTA in examining first order transitions are the pronounced effects of thermal history and sample size and packing on the results. Also the heat transfer through the thermocouple leads and the difficulties involved in centering them in each case make the technique more troublesome. If the samples were fused and pressed into

pellets in a jig which would allow for reproducible annealing and cooling of the sample and also allow a fine thermocouple to be positioned in the melt and thus become fixed in position in the pellet, these difficulties would be greatly overcome. This technique would be no more troublesome than grinding the samples to a uniform size before running a test and it would go a long way to ensuring homogeneous samples (due to pressure exerted on the melt as it is annealed and cooled most of the entrapped air should be removed) along with a reproducible position of a fine thermocouple.

The interpretation of the thermogram is another area which could use more study (chiefly from the stand point of heat transfer analysis to give a means of determining the transition temperature more accurately) and to give a firmer basis for the correlation of peak areas to enthalpies of melting or crystallization. This type of analysis will probably be carried out in the near future.

2. Accuracy

a. General

Most literature works make no reference to the accuracy of the determination of T_m or T_c using DTA, and usually only show one set of data at any given set of conditions so the data reproducibility cannot be ascertained. However, those authors who have determined them, report data reproducibilities of from ± 0.1 (109) and ± 0.5 (38, 39) up to ± 1.0 (40, 83), all values being in degrees centigrade. These are quite reasonable for polymer work where a number of morphological factors may reduce the accuracy to a much greater degree.

b. Experimental

The examination of the melting points of polyethylenes P and Q agree quite well with Holden's values, considering the differences in equipment used. It is felt from this work that values of T_m obtained using the Thermo-analyser may be quoted to $\pm 1^\circ\text{C}$. The larger differences seen from the work on polyethylene Q may be explained by differences in pretreatment. The samples used in this work were annealed at a higher temperature than those used by Holden, although this was not realized at the time the tests were carried out.

3. Usefulness

DTA can indicate melting or crystallization temperatures to within $\pm 1^\circ\text{C}$., and can be used for such purposes as:

a. Quality control of resin production

The use of a test whereby the samples were preconditioned the same way and to the same extent each time and then tested for melting point and range could show up large differences in such items as molecular weight or branching by their effects on the crystalline structure. The chief problem in this type of test would be one of sampling.

b. Information on the processing characteristics of a resin

Because of the rapidity of the test a number of melting points or crystallization tests could be carried out under different conditions to find the most effective processing conditions.

c. Quality control on finished goods

A correlation often exists between the crystalline structure and mechanical

and optical properties of polymers. Thus an analysis of crystallinity could possibly lead to better control of these other factors in molded items or in films.

C. The Uses of DTA in Examining Second Order Transitions

1. Difficulties Encountered

The chief difficulty in differential thermal analysis of second order transitions is in the interpretation of the thermogram. Base line wander and the small thermal effect of the transition make interpretation difficult. A sample preparation means, such as that described in part A, would probably reduce this baseline wander. Also a better furnace design to provide more even heat, along with a better control of the gas distribution system to provide even gas flow, would eliminate the effects of convection currents in the apparatus. If some means becomes available to produce an even heat flux, it should not be any problem to amplify the signal from the differential thermocouple to obtain more accurate results.

For second order transitions even more than for first order transitions work is necessary on the theory of heat transfer in the sample undergoing a transition. The necessity of additional accuracy in the thermogram makes this work necessary.

2. Accuracy

a. General

Because of the very small temperature differential developed by the glass transition, the precision of the DTA apparatus is extended to its extremes in measuring the transition. This naturally leads to inaccuracies. Values of

T_g (indicated) have been quoted in the literature with reproducibilities of $\pm 1.5^\circ \text{C}$. (53, 90) and $\pm 3^\circ \text{C}$. (109).

b. Experimental

The glass transition determinations on the polystyrene samples show a consistency of $\pm 1^\circ \text{C}$. However, the literature values cover such a wide range that no good comparisons could be made to check the accuracy of the tests.

The transition temperatures found for the copolymers are good to only $\pm 5^\circ \text{C}$. because of the poor thermograms produced. To get accurate results (good thermograms), the existing equipment would have to be modified or new equipment built to allow equilibrium cooling of the block.

3. Usefulness

If suitable accuracy and resolution of the thermogram could be obtained, the DTA could be used much as indicated for first order transitions only for amorphous polymers.

a. Quality control

The extent of variation of the glass transition temperature would indicate the variations present in molecular structure.

b. Information on the processing characteristics of resins

The location of the glass transition temperature is necessary for obtaining molding conditions, and the effect of various plasticizers on the transition temperature is very important and can be determined by DTA.

D. Interpretation of the Thermograms

It is felt that the analog program proposed is better than any heat transfer

theory proposed to date. It is sufficiently accurate to show that the scatter of the data on the polystyrene samples is greater than the theoretical effect of heating rate. However, if more accurate DTA equipment is developed the heat transfer in the sample undergoing the transition will have to be more critically examined, especially to consider the three dimensional effects and to investigate further the type of change the thermal diffusivity actually undergoes.

E. Uses of DTA for Polymer Analysis

DTA can be effectively used for the analysis of unknown polymer systems provided a good file of complete thermograms of known systems is available for comparison with the complete thermogram of the unknown system. All the tests on the known and unknown materials should be carried out under the same conditions of pretreatment, initial temperature and heating rate, but this is often quite difficult. A polymer like polyethylene will decompose at temperatures below those that PTFE melts at. Therefore a set of tests, possibly three to five, should be set up and initial judgement used as to which test should be tried. The test file could be set up to overlap systems between test types to a degree depending upon their melting points and decomposition points. The use of the jig described in section A for making up sample pellets could also be used in analysis to ensure even pretreatment.

F. Uses of DTA of the First Order Transition for Polymer Analysis

If the components of the polymer system are known but the percentage composition is not, analysis by using the first order transition temperature and

comparing it to theoretically or empirically derived curves of T_m v.s. composition should be an effective means of analysis. Pretreatment of the samples must be the same in every case, and must also be the same as that for any samples used to make up empirical curves. This could be accomplished by the use of a jig for making up sample pellets.

G. Uses of DTA of the Second Order Transition for Polymer Analysis

Only two valid conclusions can be drawn from the attempted copolymer analysis using the glass transition.

1. Better theoretical correlations must be obtained before this type of analysis can be of any benefit. None of the literature data or the data produced in this work correlated at all well with any of the theoretical curves. The one exception to this comment is the work of Wood (see figure 36) but these graphs show only three points, and on the other plot (figure 33) these data are no better than any of the other points.

2. At the present state of knowledge and equipment refinement, the glass transition should not be used as an analytical tool for investigation of the composition of copolymer systems. It is much better to attempt this type of analysis using the first order transition.

H. Future of DTA in the Field of Polymer Science

DTA tests are rapid and, if interpreted with a reasonable degree of understanding, quite accurate. For this reason the uses of DTA should continue to increase and the quality of the data obtained should continue to improve. As DTA equipment becomes more refined, many questions regarding

the molecular structure of polymers may be answered by application of this technique. The effects of molecular variables on crystallinity may be examined by their effect on the melting temperature and the heat of fusion of the polymer. The characteristics of the molecular variables in the amorphous region may be clarified by work on the glass transition using DTA.

Also, the time is close at hand when DTA may be used for quality control work in all phases of the polymer industry, from the synthesis of the polymer to the making of the finished goods. (Du Pont's Sabine River Polyethylene Works at Orange, Texas is currently using DTA to obtain densities of the resins produced as a quality control measure.) This will be another step from the original "eyeball" or trial and error methods towards scientific production of plastic goods.

XI

NOMENCLATURE

A	Area under the peak on a thermogram
B	"Interaction Energy Density" in equation 20
C_i	The mole fraction of homopolymer unit i
C_p	Specific heat
C_{pT_g}	Specific heat at the glass transition temperature
G	Gibbs Free Energy Function
H	Enthalpy
H_c	Molar Cohesive Energy
K	Constant
M_i	Molecular weight of homopolymer unit i
P	Packing Coefficient
R	Gas Constant
S	Entropy
T	Temperature
V	Molar volume
W_i	Weight of homopolymer unit i
X	"Thermodynamic Interaction Parameter" in equation 20
X_a	Fraction of Crystallizable units
a	Outside radius of a cylinder
f	Volume fraction of free volume in polymer molecular matrix
k	Thermal diffusivity
m	Heat transfer through thermocouple leads
n	A number analogous to the number of degrees of freedom
p	Pressure
r	Radius
t	Time
t_i	Time lag between time the surface of a cylinder reaches T_g and the time the center reaches T_g
v	Volume
\propto	Root of the Bessel Function of zero order
β	Heating rate
λ	Thermal Conductivity
ϕ	Volume fraction of diluent present in a system
η	Viscosity

Subscripts

R	Property of the reference material in the DTA assembly
S	Property of the sample material in the DTA assembly
c	Property of the crystallization transition
g	Property of the glass transition
m	Property of the melting transition
o	Property at the center of a cylinder
r	Property at radius r of a cylinder

Superscripts

o	Property of a perfect crystal
i	Property of the occupied volume fraction in the polymer molecular matrix

XII

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APPENDIX ONE

GLASS TRANSITION TEMPERATURES

POLYMER: POLYSTYRENE		T _g °C.	Type of Test	Other Factors	Reference
Sample					
Solution polymerized		100	Dilatometry		A 3
Bulk polymerized		108.5	"		"
Mn	2300	68	Calorimetry		A 18
	3370	70	"		"
	3650	82	"		"
		82			A 19
Molded from pellets		79-81	Ultra-sonic frequency		
$\bar{M} = 3.2 \times 10^5$			& Dilatometry 10°C/Hr.		A 20
Mol. Wt.					
	85,000	100	Capillary viscosities		A 21
	19,300	89	"		"
	13,300	86	"		"
	6,650	77	"		
	4,980	78	"		
	3,590	75			
	3,041	65			
	2,600	62	"		"
all above were bulk polymerized					
Dow 19F	\bar{M}_w 370,000	100	Dynamic Mechanical		
			30 to 1500 cps		A 22
		100	Dilatometry		A 23
Amorphous Isotactic		97	Stress-strain	10 sec. modulus	A 24
Atactic		95	"	"	"
Mol. Wt.	24,000	95	Dilatometry		A 51
		100	Dynamic Mechanical		A 52
					54
					55
					56
					58
Dow 666K		83	DTA		A 63

POLYMER: POLYMETHYL METHACRYLATE

Sample	T _g °C.	Type of Test	Other Factors	Reference
	110	DTA	Rate extrapolated to zero	A 36
	110	Stress-strain	Equilibrium	A 4
Made by author	105	Dilatometry		A 25
	109	Stress-strain	10 sec. modulus	A 24
Molecular Weight $\overline{M}_n \times 10^{-3}$	°K			
2.74	323.6	Refractometry		A 38
2.96	340.5	"		"
4.38	350.0	"		"
9.12	364.3	"		"
11.2	369.0	"		"
12.5	370.3	"		"
15.9	374.7	"		"
19.4	375.7	"		"
19.7	376.7	"		"
21.9	374.0	"		"
23.7	378.5	"		"
25.9	376.0	"		"
27.8	378.0	"		"
28.8	376.8	"		"
29.8	379.8	"		"
34.6	380.5	"		"
35.2	380.8	"		"
37.6	380.0	"		"
72.4	384.6	"		"
74.4	374.5	"		"
76.6	383.5	"		"
Cross-linked	105	Viscosities		A 25
unspecified	105	Dilatometry		A 40
Mol. Wt. 61,500	100	Dynamic Mechanical		A 41
	78	Refractometry		A 39
	83			A 42

POLYMER: POLYMETHYL METHACRYLATE

Sample	Tg°C.	Type of Test	Other Factors	Reference
	111	Stress-strain		A 43
	115	NMR		A 44
Syndiotactic ρ @ 30°C. g/m l.				
1.19	115	Dilatometry	Rohm & Haas	A 8
Isotactic 1.22	45	"	" Co.	"
Isotactic-Syndiotactic Block				
1.20 - 1.22	60-95	"	"	"
Conventional 1.199	104	"	"	"
Mol. Wt. 12,000 - 30,000	100	Dilatometry	Tg° = 105°C.	A 51
	112	Dynamic Mechanical		A 52 54 55 56 57 58
Lab Sample	111	DTA		A 63

POLYMER: POLYPROPYLENE

Atactic	-10	Dilatometry	Equilibrium	A 36
	- 8.4	DTA	Extrapolated	"
	-18	Stress-strain	10 sec. mod.	A 24
% cryst.	Ave. Tg			
amorphous	-34.5	Dilatometry		A 47
80	-35			
65	-37			
50	-36			
45	-34.5			
amorphous	-35.5			
35	-36			
85	-34.5			
75	-35.5	"		

POLYMER: POLYPROPYLENE

Sample		T _g °C.	Type of Test	Other Factors	Reference
Atactic	$\bar{M}_n =$				
	3,000	-35	DTA		A 50
	6,000	-19	"		"
	10,000	-17, -22	"		"
	15,000	-12	"		"
	20,000	-14, -18	"		"
	50,000	-10	"		"
	150,000	-9	"		"
	750,000	-8	"		"
	1,000,000	-7	"		"
		-13	Dynamic Mechanical		A 53 58

POLYMER: POLYVINYL CHLORIDE

General Electric SN-85114	78.5 80	Calorimetry "	Equilibrium "	A 28 "
Polymerization Temp. °C.				
125	68	Stiffness modulus		A 37
90	75	and mechanical loss		"
40	80	"		"
-10	90	"		"
-80	100	"		"
	74	Dynamic Mechanical		
			0.7 C.P.S.	A 52 58
Marvinol VR-10	80.5	DTA		A 63
Lab. Sample	74	"		"

POLYMER: POLYVINYL ACETATE

Sheet containing no plasticizer,
filler or other material

30	Dielectric loss	10^{-2} cps	A 8
20	"	10^{-4} cps	"
13.2	"	? very slow	"
30	Dilatometry	0.3°C./min	"

POLYMER: POLYVINYL ACETATE

Sample	T _g °C.	Type of Test	Other Factors	Reference
Block polymerization	28	Dilatometry		A 20
	26	Stress-strain	30 Kc	"
Made by author in Lab.	29	Refractometry		A 27
	30	Dynamic Mechanical		A 52 54 58
	30			A 61

POLYMER: NYLON

Nylon 6	46	Stress-strain		A 24
Nylon 66	46	"		"
Nylon MXD-6	46	"		"
Nylon 6 industrial	-65	Penetrometer	0.5°C./min	A 29
Nylon 66 industrial	-65.5	"	"	"
Du Pont Nylon 6 Flake, \overline{M}_n 20,000	45-48	Calorimetry	Equilibrium	A 30
Undrawn yarn, \overline{M}_n 18,500	31	"	"	"
Drawn yarn, \overline{M}_n 18,500	38	"	"	"
Above only melt annealed	20	"	"	"
Nylon 66	70	Dynamic Mechanical		A 53 58

POLYMER: POLY ACRYLONITRILE

	68	Dielectric loss		A 8
	130	Dilatometry		A 3
Made by author \overline{M}_n 1.3×10^5	104	Dilatometry	4°C./hr.	A 31

POLYMER: POLY ACRYLONITRILE

Sample	T _g °C.	Type of Test	Other Factors	Reference
Aqueous Polymerized 50°C.	87, 86	Coeff. Thermal Expansion	1°C./min.	A 60
	92, 103	"	"	"
Mol. Wt. 1,500 - 2,000	56	DTA		A 63
2,600				
8,500	73	"		"
60,000	74	"		"
200,000	80.5	"		"
7,300,000	79	"		"

POLYMER: POLYETHYLENE TEREPHTHALATE

	68	Dielectric loss		A 8
Powdered to 36 mesh sieve	70	DTA	4.5°C./min	A 32
	72	Dynamic Mechanical		A 53 58

POLYMER: POLYCHLOROTETRAFLUOROETHYLENE

	-20	Dilatometry	0.3°C./min	A 8
	-20	Dielectric loss		"
Powdered Kel-F, high M. Wt.	-90	Calorimetry		A 33
	-120	"		"
	76	Dynamic Mechanical		A 53 58

BUTYL POLYMERS

Polyisobutylene	-66	Stress-strain	10 _{sec.} modulus 10 ⁹ dynes/cm ²	A 24
Polybutene-1	-25	Dilatometry		A 34
Hevea Rubber (Unvulcanized)	-73	Dynamic Mechanical	1.2 C.P.S.	A 52 58

POLYMER: POLYURETHANE

Sample	Tg°C.	Type of Test	Other Factors	Reference
Vulcollan 18/40 M. Wt. 2,000	-40	Stress-strain		A 35

POLYMER: POLYETHYLENE

Phillips Marlex 50	-130	Volume change from unit cell by X-ray 5° steps		A 45
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Melt Index		Mnx10 ⁻³				
Du Pont						
A	0.2	34	-24.2	Dilatometry	-0.3°C/min	A 46
B	2.1	32	-25.8	"	"	"
C	2.1	21	-28.8	"	"	"
D	2.1	18	-32.5	"	"	"
E	3.8	20	-26.3	"	"	"
F	2.0	50	-27.3	"	"	"
G	1.8	27	-22.2	"	"	"
H	1.6	12	-34.0	"	"	"
Marlex 50-9			-18	"	"	"
Zeigler			-20	"	"	"
			-20	Dynamic Mechanical		A 53 58

COPOLYMER	Sample	T _g °C	Type of Test	Other Factors	Reference
Butadiene-Styrene	Gr*S (standard) 0.245 polystyrene	-56	Dilatometer with air as confining fluid		A 1
		-64			
	"	-54	Dilatometer w / 38% H ₂ SO ₄ confining fluid		A 2
	"	-53	Stress-strain @ equilibrium		A 4
	NE 441 0.41 polystyrene	-23	Dilatometry w / mercury		A 3
	NS 662 0.43 polystyrene	-21	Dilatometer w / mercury		A 3
	National Bur. Standards 0.43 polystyrene	-23	Dilatometer w / air		A 1
	gum vulcanates of butadiene-styrene containing				
	40 wt. % styrene	-39.1	stress-strain		A 5
	50 wt. % styrene	-22.2	"		"
	60 wt. % styrene	12.1	"		"
	Emulsion polymerized Wt. % polystyrene				
			Polymerization Temp. (°C.)		
- 0.0		-75	Dilatometer	-20	A 9
6.8		-71.5	"	-20	"
23.0		-62.5	"	-20	"

COPOLYMER	Sample	T _g °C.	Type of Test	Other Factors	Reference
Butadiene -Styrene	Wt.% Styrene				
	0.0	-79	Interferometer	5	A 10
	2.5	-74	"	5	"
	8.6	-70	"	5	"
		-74	"	50	"
	22.6	-52	"	51	"
	24.0	-56	"	50	"
	36.3	-38	"	5	"
	43.0	-34	"	50	"
	53.1	-14	"	5	"
	55.7	-13	"	50	"
	44 (commercial)	-28	"	50	"
	65 "	- 2	"	50	"
	75 "	13	"	50	"
	80 "	21	"	50	"
	85 "	36	"	50	"
	0.0	-78	Calorimetry	5	A 11
	"	-86	"	50	"
	8.6	-80	"	50	"
	43	-36	"	50	"
GR-S X387	22	-67	Refractometer		A 14
GR-S X387 - Extracted with ETA		-65	"		"
GR-S	25.5	-61	Calorimetry		"
Goodrite 50	85 (Assume Wt.%)	40	Refractometer		A 15
Mol. Wt. Monomer	Styrene				
56.5	8.58 (Assume Wt.%)	-80			A 18
60.7	22.61	-60			"
61.5	25.5	-59			"
68.2	42.98	-36			"
Butadiene -Acrylonitrile	Wt. % AN				
	39	-23	Calorimetry and dilatometry		A 12
	40	-22	Interferometer		A 13
Enjay Co. Inc.	% AN	% N ₂			
Perbunam 18	20.1	5.31	-56	Refractometer	A 16
Perbunam 26NS60	28.6	7.55	-46	"	"

COPOLYMER	Sample		T _g °C	Type of Test	Other Factors	Reference
Butadiene						
-Acrylonitrile	% AN	% N ₂				
Perbunam						
35NS90	36.6	9.66	-34	Refractometer		A 16
B.F. Goodrich Chem. Co.						
Hycar OR25	32.8	8.66	-37	"		"
Hycar OR15	39.0	10.3	-26	"		"
Xylos Rubber Co.						
Butadiene						
Butaprene						
NF-NSP75	22.4	5.91	-52	Refractometer		"
Butaprene						
NL	30.2	7.97	-41	"		"
Butaprene						
NL-NSP84	26.2	6.91	-50	"		"
Butaprene						
NAA	33.4	8.81	-39	"		"
Butaprene						
NXM	39.1	10.3	-33	"		"
Butaprene						
20-90	52.0	13.7	-16	"		"
Goodyear Tire and Rubber Co.						
Chemgum N4NS						
	30.8	8.13	-43	"		"
" N3	39.5	10.4	-32	"		"
" N3NS	39.7	10.6	-27	"		"
Paracril A						
0.216 acrylonitrile			-43	Dilatometer w / 38% H ₂ SO ₄		A 3
Paracril B						
0.26 AN			-39	Dilatometer w / 38% H ₂ SO ₄		"
Paracril C						
0.351 AN			-30.0	"		"
			-29.5	Dil. w / mercury		"
Paracril 35						
0.35 AN			-25	stress-strain	1°/4 hrs.	A 6

COPOLYMER	Sample	T _g °C.	Type of Test	Other Factors	Reference
Acrylonitrile - Styrene					
Mole % Acrylonitrile	Type of Polymerization			η @ 25°C.	
1.00	Benzene	92.0		1.5187	A 59
.962	Bulk	94.0		1.5123	"
.939	Benzene	95.3		1.5258	"
.927	Bulk	81.0		1.5233	"
.913	Benzene	86.3		1.5270	"
.900	"	88.0		1.5309	"
.878	"	97.2		1.5284	"
.867	"	85.2		1.5319	"
.852	"	89.0		1.5346	"
.825	"	91.7		1.5338	"
.816	"	81.0		1.5341	"
.808	Bulk	98.3		1.5366	"
.750	"	98.0		1.5418	"
.743	Benzene	98.7		1.5454	"
.690	"	98.0		1.5495	"
.672	"	98.5		1.5478	"
.604	"	106.2		1.5514	"
.588	Bulk	103.6		1.5550	"
.580	Benzene	103.8		1.5533	"
.469	"	104.9		1.5615	"
.460	Bulk	102.0		1.5665	"
.449	Benzene	101.0		1.5625	"
.266	Bulk	99.0		1.5734	"
.263	Benzene	95.4		1.5743	"
.213	Bulk	94.2		1.5763	"
.084	"	95.2		1.5822	"
.061	"	96.8		1.5862	"

Acrylonitrile - Vinyl Acetate

Aqueous solution polymerized
@ 50°C.

Wt. Fraction V.A.				
0	87, 86	Coeff. of	1°C./min	A 60
0.02	86	Thermal	"	"
0.05	79, 85, 86, 84	Expansion	"	"
0.06	87	"	"	"
0.08	86	"	"	"
0.10	76	"	"	"
0.16	81	"	"	"

<u>COPOLYMER</u>	<u>Sample</u>	<u>Tg° C.</u>	<u>Type of Test</u>	<u>Other Factors</u>	<u>Reference</u>
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Acrylonitrile - Vinyl Acetate

Wt. Fraction V.A.

0.27	84	Coeff. of	1°C./min	A 60
0.32	80	Thermal	"	"
0.38	75	Expansion	"	"
0.43	70	"	"	"
0.58	65	"	"	"
0.64	58	"	"	"
1.00	30	"	"	A 61

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